अवअयस्क रेफिनेट से धातु मानों की प्रतिप्राप्ति

1

खोखले फाइबर संस्पर्शित्र में आलंबित तरल झिल्ली के माध्यम से विलयन परिवहन का अनुकरण करने के लिए जीयूआई के साथ कोड का विकास एवं सत्यापन

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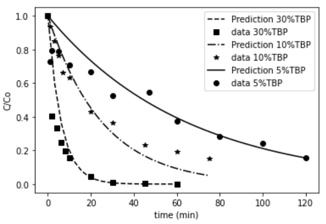

डेटा वेल्यू के साथ यू (VI) निष्कर्षण के लिए जी. यू. आई. के साथ कोड का सत्यापन

सारांश

खोखले फाइबर संस्पर्शित्र में प्रयुक्त तरल झिल्ली के उपयोग से विलायक निष्कर्षण प्रक्रमण की तीव्रता के उदाहरणों में से एक है। इस प्रक्रिया द्वारा धातु परिमाणों से क्षीण अम्लीय रेफिनेट का कुशलता से विवेचन किया जा सकता है। यह प्रक्रिया परिमाण प्रतिप्राप्ति और रेफिनेट के कुशल विवेचन, दोनों मामले में लाभदायक है। प्रक्रिया के अभिकल्पन और पैमाने में वृद्धि हेतु खोखले फाइबर संस्पर्शित्र में सहयोगी/जड़ तरल झिल्ली के माध्यम से द्रव्यमान परिवहन का एक गणितीय मॉडल विकसित किया गया है। वर्तमान शोध-पत्र में, मॉडल समीकरणों को हल करने के लिए ग्राफिकल यूज़र इंटरफेस (जीयूआई) के साथ एक कोड विकसित किया गया है और विभिन्न धातु आयनों जैसे कि U(VI), Pu(IV), Cs(I) और Cr(VI) का परीक्षण किया गया है। जीयूआई के साथ कोड धातु आयनों की विभिन्न प्रणालियों, उनके लिगेंड, द्रव-गतिकी स्थितियों एवं संस्पर्शित्र की विशेषताओं आदि के लिए प्रक्रिया की पूर्वानुमान की सुविधा प्रदान करता है।

Recovery of Metal Values From Lean Raffinates

1

Development and Validation of a Code with GUI to Simulate Solute Transport through Liquid Membrane Supported in Hollow Fibre Contactor

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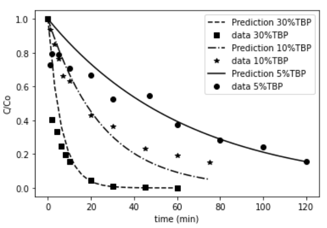

Validation of the code with GUI for U(VI) extraction using data

ABSTRACT

Solvent extraction using liquid membrane employed in hollow fibre contactor is one of the examples of process intensification. Acidic raffinates lean in metal values, can be efficiently treated with this process. This process is advantageous in terms of both value recovery and efficient disposal of the raffinate. A mathematical model of the mass transport through liquid membrane supported/immobilized in hollow fibre contactor is developed for design and scale-up of the process. In the present work, a code with graphical user interface (GUI) is developed to solve the model equations and tested for different metal ions viz. U(VI), Pu(IV), Cs(I) and Cr(VI). The code with GUI facilitates prediction of the process for different systems of metal ions, their ligands, hydrodynamic conditions and contactor characteristics etc.

KEYWORDS: *Graphical user interface, Hollow fibre contactor, Liquid membrane, Modelling.*

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Introduction

Hollow fibre liquid membrane process is beneficial for treatment of lean acidic raffinates over conventional process because of its higher interfacial area, non-dispersive contact, modular design and low solvent inventory. Hollow fibre module is a shell and tube type mass transfer contactor, in which a number of thin microporous polymeric fibres are systematically packed in a shell. A fibre is a thin hollow cylinder with wall made of microporous polymer. In the mass transfer process employing hollow fibre contactor, feed flows inside the fibres and strippant flows on the shell side while organic liquid membrane resides in the micropores of the fibre wall. Aqueous-organic interfaces exist at pore mouths. Because of this configuration, simultaneous extraction and stripping occurs at these interfaces. The developed model predicts mass transfer of the metal ion through liquid membrane, for varying operational parameters, using differential mass balance of the solute along a single fibre lumen considering fast interfacial reaction coupled with the solute fluxes through phase interfaces. The details of the model are discussed elsewhere [1]. In this work, a graphical user interface (GUI) of the code to solve the mass transfer model equations is developed. This work is part of ANUSim module development [2] to facilitate prediction of solute transport in solvent extraction contactors.

Methods

The source code of GUI is developed in Python 3.0 interpreter. It predicts concentration profile of metal ion on providing user inputs viz. contactor characteristics (fibre inner and outer diameters, fibre porosity, tortuosity, fibre wall thickness and fibre length), flow rates, distribution coefficients and metal ion diffusivities in aqueous films and organic membrane. Distribution coefficients of metal ions in organic liquid membrane are taken from literature [3, 4]. Individual mass transfer coefficients of feed (aqueous), membrane (organic) and strip (aqueous) are estimated from the reported correlations [5-7] using system parameters. Parameters used for prediction are compiled in Table 1. Experimental data for validation of the model are taken from literature for U(VI) [8-9], Pu(IV) [10], Cs(I) [11] and Cr(VI) [12].

The code with GUI shows the progress of the mass transport with time (t)/ lumen length (z) in terms of concentration profile of the metal ion. Mass transfer coefficients are estimated and displayed in the GUI. Bench-marking of the code with GUI is done for extraction of different metal ions viz. U(VI), Pu(IV), Cs(I) and Cr(VI).

Results

Fig.1 presents the result of the case study of uranium extraction using the GUI code. Fig.1a shows the prediction made by the model along with the experimental data [8] for different carrier (TBP/ dodecane) concentrations. As carrier concentration increases, rate of uranyl ion transport also increases because of increase in distribution coefficient K_d. Mass transfer coefficient, k_m, decreases with increase in carrier concentration because of increase in viscosity of organic membrane and therefore beyond certain value, increase in carrier concentration will not lead to increase in solute transport in spite of increase in K_d. The predictions are made by using K_d and k_m accordingly as input in the code. Fig.1b presents the plot of model prediction and reported data [9] of uranium transport for a different system having feed acidity of 3N and different strippant with a different hollow fibre contactor having different characteristics. Fig.2 shows the results of plutonium separation for contactor characteristics and system composition given in Table 1 for which model predictions are found in agreement with the reported data [10]. Fig.3 presents the results of the case study of extraction of cesium. Fig.3a shows the prediction of change in dimensionless concentration in feed with time for different feed metal ion concentrations along with the experimental data [11]. As metal ion concentration increases, free carrier concentration decreases at the reaction interface, resulting in decrease in distribution coefficient, K_d at equilibrium. This decrease in K_d leads to decrease in rate of transport as shown in Fig.3a. Model predictions also follow the same trend when varying input value of K_d (shown in Table 1) is used accordingly while executing the code. Figure 3b shows prediction for different feed flow rates along with the experimental data [11]. Prediction (Fig.3b) shows no effect of change of flow rate on metal ion transport (using input of different feed film coefficient, k_f as per different feed flow velocities, v_f). Similar trend of insignificant effect of feed flow rate on extraction has been observed in the experiments [11] and is attributed to the transport rate being membrane diffusion controlled. Fig.4

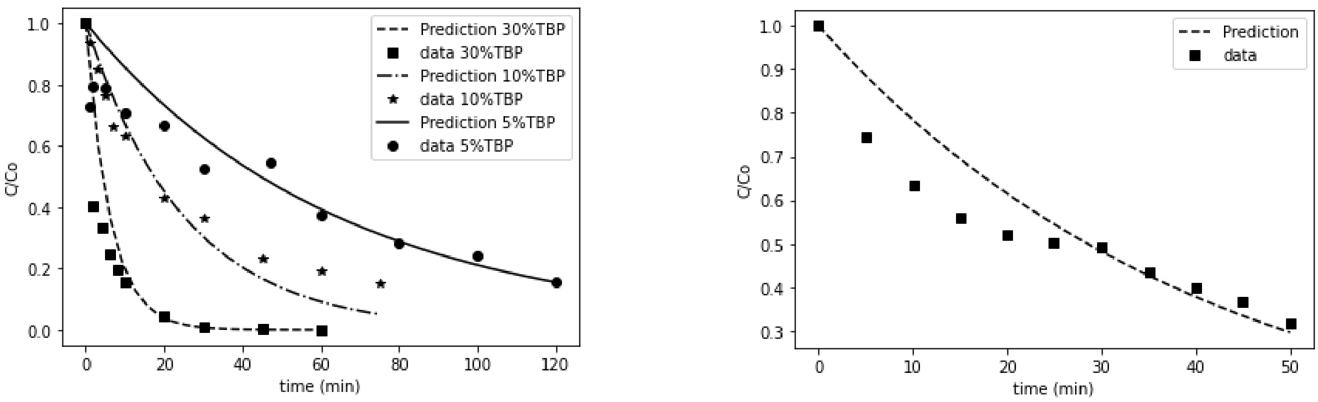

Fig.1: Validation of the code with GUI for U(VI) extraction for (a) data reported in [8], (b) data reported in [9]. The input parameters for the two cases are listed in Table 1.

Table 1: Parameters used for validation case studies

Input Parameters	U(VI)		Pu(IV)	Cs(I)		Cr(VI)
	Case study 1a [8]	Case study 1b [9]	Case study 2 [10]	Case study 3a [11]	Case study 3b [11]	Case study 4 [12]
Fiber outer radius, r_o/ inner radius, r_i (cm)	0.015/ 0.012	0.05/ 0.03	0.05/ 0.03	0.015/ 0.012		0.015/ 0.012
Feed flow rate (ml/min)	400	3	3	200	200, 300, 400	840
Feed volume (ml)	500	25	25	500		2000
Feed flow velocity (cm/s)	1.48	0.885	0.885	0.737	0.737, 1.106, 1.4743	3.09
Fiber porosity, ε	0.4	0.7	0.7	0.4		0.4
Fiber Pore size (cm), d_p	0.05×10^{-04}	0.2×10^{-04}	0.2×10^{-04}	0.03×10^{-04}		0.03×10^{-04}
Fiber wall thickness, L (cm)	0.003	200×10^{-04}	200×10^{-04}	0.003		0.003
Fiber length, l (cm)	15	10	10	15		15.6
Initial feed metal ion concentration, C_o	0.4 gpl in 1 N HNO_3	4.6×10^{-03} gpl in 3 N HNO_3	8×10^{-03} gpl in 3 N HNO_3	Tracer (1×10^{-07} M), 0.1 gpl in 3 N HNO_3	Tracer (1×10^{-07} M) in 3 N HNO_3	0.05-6 gpl at pH 1.5 (0.015N H_2SO_4)
Carrier concentration	30, 10, 5 % v/v TBP/ dodecane	30 % v/v TBP/ dodecane	30 % v/v TBP/ dodecane	1 mM CNC/ 80% NPOE in dodecane		0.213 M secondary amine in Isopar L
Strippant	1 M Na_2CO_3	0.1 M $NH_2OH.HCl$ in 0.3 M HNO_3	0.1 M $NH_2OH.HCl$ in 0.3 M HNO_3	Distilled water		3 M NaOH
Distribution coefficient, K_d	7.66, 1.25, 0.34	26	16	2.13, 1.15	2.13	K_d is function of C_f as, $K_d = -85\ln(C_f)+1092$
Feed film coefficient (cm/s), k_f by Leveque correlation $Sh=1.62\left(\frac{4r_i^2 v_f}{l\,D_{aq}}\right)^{1/3}$ [5]	1.714×10^{-03}	1.218×10^{-03}	1.218×10^{-03}	3.0858×10^{-03}	3.0858×10^{-03}, 3.53×10^{-03}, 3.882×10^{-03}	2.22×10^{-03}
Membrane mass transfer coefficient (cm/s), k_m by $k_m = \frac{D_{org}}{L}$ [6,8]	4.733×10^{-05}, 5.6×10^{-05}, 5.8×10^{-05}	1.737×10^{-05}	5.85×10^{-05}	1.467×10^{-05}		3.251×10^{-05}
Strip film coefficient (cm/s), k_s by $\frac{k_s}{v_s} Sc^{0.67} = 3.42\, Re^{-0.672}$ [7]	6.33×10^{-03}	1.144×10^{-03}	1.144×10^{-03}	1.1445×10^{-02}		9.3×10^{-03}

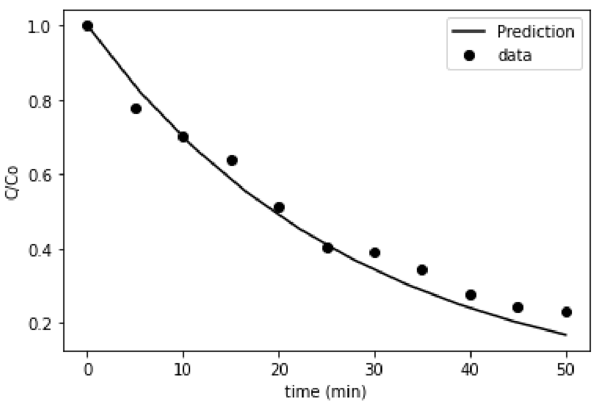

Fig.2: Validation of the code with GUI for Pu(IV) extraction using reported data [10]. The input parameters are listed in Table 1.

shows prediction of chromium flux for different feed chromium concentration with corresponding reported data [12]. As flux is directly proportional to the concentration gradient, increase in feed chromium concentration leads to increase in the flux. Deviation between prediction and data is found ~15% for these case studies. Deviation between model prediction and data is calculated as,

$$\text{Deviation}\,(\%) = \frac{100}{p}\sum_{m=1}^{p}\left(\frac{\left|y_{\text{Expt},m} - y_{\text{Pred},m}\right|}{y_{\text{Expt},m}}\right)$$

Where, *p* stands for number of data points and y represents data values. Fig.5 shows the screenshot of the graphical user interface (GUI). The left side of the GUI is for providing user *input parameters*. The lower middle frame provides the tabs for

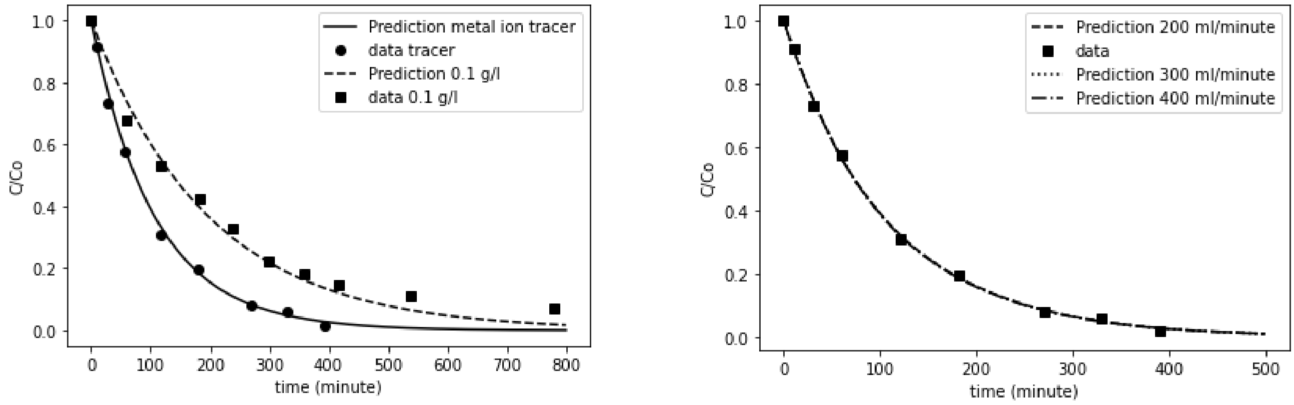

Fig.3: Validation of the code with GUI for Cs(I) extraction for (a) different feed metal ion concentrations (data reported in [11]), (b) different feed flow rates (data reported in [11]). The input parameters are listed in Table 1. Metal ion tracer concentration is 1x10^{-07} M.

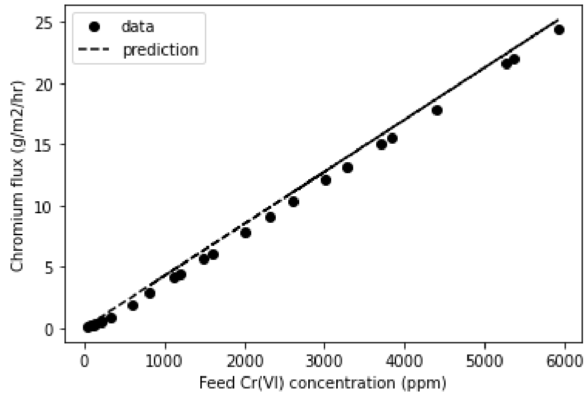

Fig.4: Validation of the code with GUI for Cr(VI) extraction using reported data [12]. The input parameters are listed in Table 1.

calculating mass transfer coefficients and Reynolds numbers after the input parameters have been specified by the user. Pressing the button show graph displays the results in the graphical form on the right side of the GUI. The results obtained from solution of the model equations for the provided user inputs are shown graphically. There is provision to display plots of prediction for both re-circulating (RC) mode and once through (OT) mode.

In re-circulating (RC) mode, feed is re-circulated through hollow fiber lumen for a definite time, while in once-through (OT) mode, feed is only once passed through the hollow fiber lumen. RC mode displays dimensionless feed concentration in the feed reservoir and % extraction (=100(1-(C/C_o))) versus time, while OT mode displays % extraction versus length of the lumen.

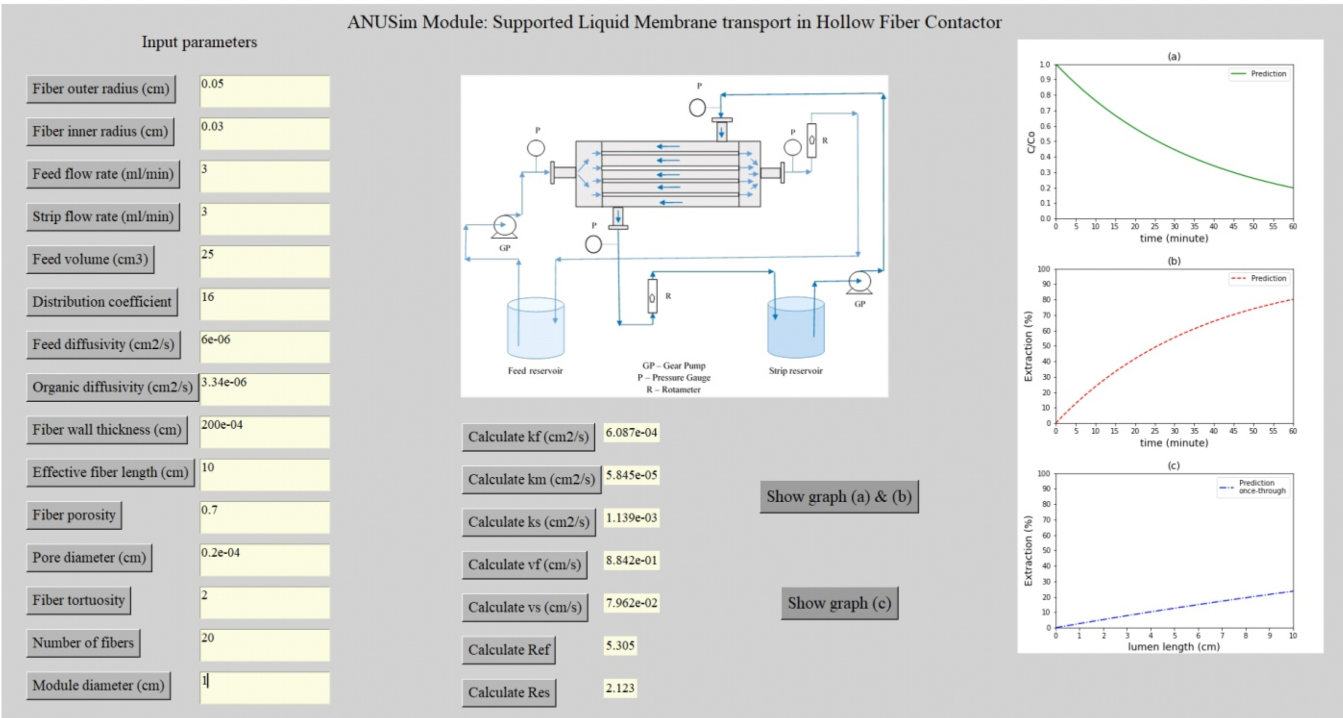

Fig.5: Screenshot of the developed graphical user interface (GUI) of the code for simulating solvent extraction in a hollow fiber module.

Conclusions

Solvent extraction using liquid membrane in hollow fibre membrane contactor is promising for recovery of metal values from lean raffinates. Mathematical model of solvent extraction using liquid membrane in hollow fibre membrane contactor is beneficial for prediction of mass transport process prior to experimental runs. In this work, a code with GUI is developed to simulate the solvent extraction in hollow fibre membrane contactor using supported liquid membrane. The GUI provides the tabs for input parameters to be provided by the user. The model equations are solved in the background and concentration profile of metal ion with respect to time or space are generated. The code with GUI has been validated for extraction of different metal ions (U(VI), Pu(IV), Cs(I), Cr(VI))) with absolute average relative deviation between the predicted and experimental results being ~15%. The code with GUI can be used for parametric analysis and design and scale-up of the process for a given separation task to be achieved using hollow fibre membrane contactor operated in supported liquid membrane mode.

Nomenclature

C feed concentration	***Subscript***
D - diffusivity	o - initial
k - mass transfer coefficient	aq - aqueous film
K_d - distribution coefficient	org - organic in pores
l - fibre/ lumen length	f - feed
v - flow velocity	m - membrane
Re, Sh, Sc - Reynolds, Sherwood, Schmidt number	s - strip

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