Optimization of cyanide extraction from wastewater using emulsion liquid membrane system by response surface methodology
Juan Qin Xue, Ni Na Liu, Guo Ping Li and Long Tao Dang

ABSTRACT
To solve the disposal problem of cyanide wastewater, removal of cyanide from wastewater using a water-in-oil emulsion type of emulsion liquid membrane (ELM) was studied in this work. Specifically, the effects of surfactant Span-80, carrier trioctylamine (TOA), stripping agent NaOH solution and the emulsion-to-external-phase-volume ratio on removal of cyanide were investigated. Removal of total cyanide was determined using the silver nitrate titration method. Regression analysis and optimization of the conditions were conducted using the Design-Expert software and response surface methodology (RSM). The actual cyanide removals and the removals predicted using RSM analysis were in close agreement, and the optimal conditions were determined to be as follows: the volume fraction of Span-80, 4% (v/v); the volume fraction of TOA, 4% (v/v); the concentration of NaOH, 1% (w/v); and the emulsion-to-external-phase volume ratio, 1:7. Under the optimum conditions, the removal of total cyanide was 95.07%, and the RSM predicted removal was 94.90%, with a small exception. The treatment of cyanide wastewater using an ELM is an effective technique for application in industry.

Key words | cyanide wastewater, emulsion liquid membrane, response surface method

INTRODUCTION
Cyanide wastewater is industrial wastewater containing the cyano group (Sergio et al. 2015) and arises mainly from the textiles, non-ferrous metal smelting, processing, coking, chemical, and electroplating industries, as well as from other industrial processes (Dvorak et al. 2014; Li et al. 2015). Cyanides are highly toxic because they combine with high-speed rail cytochrome, leading to tissue hypoxia and asphyxia (Dash et al. 2009). Any discharge of cyanide wastewater will do harm to aquatic organisms, livestock, and the ecological balance of receiving waters (Kuyucak & Akcil 2013; Shen et al. 2014), as well as render the waters unsafe for human consumption. Therefore, treatment of cyanide wastewater to reduce environment pollution is very important.

Many methods (Table 1) have been examined for removal of cyanide from wastewater such as photocatalytic oxidation (Baeissa 2014, 2015; Pala et al. 2015), electrodialysis (Alonso et al. 2013; Scarazzato et al. 2015; Zheng et al. 2015), ion exchange and biochemical reaction. However, these methods generate secondary pollution, have large investment costs and require harsh reaction conditions (Moussavi & Khosravi 2010; Jawale et al. 2014). To overcome such problems, a high efficiency energy-saving cyanide removal technique based on plasma discharge has been developed (Hijosa et al. 2013).

Many researchers have found that emulsion liquid membrane (ELM) extraction has a great potential for separating and concentrating metal ions in wastewater compared to solvent extraction (Eyupoglu & Kumbasar 2015). The ELM separation technique has been tested in hydrometallurgy and wastewater treatment (Othman et al. 2006; Tijing et al. 2014). ELM technology has developed rapidly since it was initially proposed by Li (Li 1968) as an improved solvent extraction (Jiao et al. 2015) technique. ELM extraction has been applied to separation of dyes (Agarwal et al. 2010; Dâas & Hamaoui 2010; Othman et al. 2011), phenols (Ng et al. 2010; Reis et al. 2011) and metal ions (Tang et al. 2010; Nosrati et al. 2011) from aqueous solutions. ELM technology has many advantages such as simplicity, improved
kinetics and good selectivity. Moreover, ELM treatment allows very high mass transfer rates due to the large surface area of the emulsion globules and internal droplets (Rajasimman et al. 2009; García et al. 2013), which enables extraction and stripping simultaneously. Thus, ELM extraction is becoming more and more important in areas such as metallurgy, medicine and biochemistry.

The purpose of this study was to determine the optimum operating variables for extraction of cyanide from aqueous solutions by an ELM. The research used response surface methodology (RSM) to examine the effects of these variables on cyanide extraction.

### EXPERIMENTAL

#### Preparation of ELM

The choice of a suitable membrane material, surfactant and the internal phase is made based on the industrial wastewater to be treated; then, a water-in-oil emulsion can be made by vigorously stirring the mixture. In this study, emulsions were prepared by emulsifying NaOH (20 mL at concentrations of 1%, 3% and 5% w/v) aqueous solutions (internal phase) in an organic membrane phase. The organic membrane phase (20 mL) was composed of paraffinic solvent (1% v/v), carrier trioctylamine (TOA) (1%, 3% and 5% v/v), surfactant Span-80 (1%, 2.5% and 4% v/v) and kerosene. Emulsification was accomplished by stirring the mixture at 2,300 rpm in a high-shear emulsifying machine with a residence time of 900 s. The emulsions were freshly prepared just prior to each extraction experiment.

#### Treatment of cyanide wastewater

The cyanide wastewater used in this study was obtained from a gold smelter. The raw wastewater was diluted a pre-determined number of times and amended with sulfuric acid to regulate pH to 4. The prepared emulsions were dispersed in many globules (0.5–3 mm diameter) into an agitated vessel with the external solution (cyanide wastewater) in a volumetric ratio of 1:5. Each globule (Figure 1) consisted of a stripping phase encapsulated in an organic membrane phase containing a surfactant. The mixture solution (cyanide wastewater and emulsions) then was quickly poured into a separation funnel, after which the organic membrane phase and water phase were immediately divided into two layers (oil phase and aqueous phase). The aqueous phase was clear and transparent, and was placed in a distilling flask for distillation, the distillate from which was analyzed to measure the total cyanide content. The analyses followed the silver nitrate titration method for determination of total cyanide in water (National Environmental Protection Agency 1987).

#### Extraction process

The emulsions consisted of a stripping solution (continuous phase), which was encapsulated in an organic membrane phase (dispersed phase) in the form of various-size droplets with the help of a surfactant (Span-80). The principle of
are presented in Table 2.

Factors and their corresponding levels were chosen as the independent variables. The ANOVA model was used to determine the optimum level of each variable for maximum response. Optimum conditions were determined using analysis of variance (ANOVA). Operating parameters were chosen as the independent variables. The levels of each variable, mean extraction and fitting relevance are presented in Table 2.

Experimental design and data analysis

Design-Expert 8.0.6 software (Stat-Ease, Inc.) was employed for the statistical design and data analysis. The response surfaces were plotted to understand the interaction of the variables and determine the optimum level of each variable for maximum response. Optimum conditions were determined using analysis of variance (ANOVA). Operating parameters were chosen as the independent variables. The levels of each variable, mean extraction and fitting relevance are presented in Table 2.

RESULTS AND DISCUSSION

RSM is a statistical experimental design to determine the optimal response of a system, such as a biological process, to various independent variables. It is commonly applied to explore the relationships between test variables and their effects on one or more response variables, and decreases the number of required experiments considerably without ignoring the interactions among the test variables (Rajasimman & Sangeetha 2009; Jiao et al. 2013). RSM can be applied through the analysis of interactions between factors and the mode of fit, and through further analysis of the extent of multi-factor influence on the response variables. In this study, the optimal experimental conditions were obtained using calculations based on mathematical theory and the reaction equation to construct three-dimensional response surface and response contours.

Table 3 shows the ANOVA model for the percentage extraction of cyanide using TOA. The ANOVA model F-value (3.67) implies the model is statistically significant and any values for ‘Prob > F’ that are less than 0.05 indicate that an associated model term is statistically significant. Thus, the regression model is highly significant. The ‘Predicted R²’ of 0.84 is in reasonable agreement with the ‘Adjusted R²’ of 0.93.

The process variables of ELM for the removal of cyanide were examined using RSM with the Box–Behnken design (described in Table 4). The regression model for the removal of total cyanide is expressed by the following equation:

\[
HCN + NaOH \rightarrow NaCN + H_2O
\]  

\[(1)\]


\[(2)\]
The response surfaces for the extraction of cyanide from wastewater by ELM treatment using surfactant Span-80 are shown in Figure 3. Each response surface represents the change in levels of two factors with the other two factors maintained at zero levels. The elliptical nature of the contours and the interaction between the individual variables is significant.

**Relationship of Span-80 content and TOA content**

Figure 3(a) shows that cyanide removal increases to a peak at a Span-80 volume fraction of approximately 2.5% and then decreases notably as the Span-80 fraction continues to increase. The bending degree of the B axis is smooth relative to that of the A axis, indicating that the effect of the volume fraction of TOA on extraction efficiency is not as significant as the volume fraction of Span-80. This can be explained by the fact that as a surfactant, Span-80 is insufficient for kerosene to surround all the internal phase when it is at low levels, leading to a less stable emulsion. As the proportion of Span-80 in the membrane increases, interfacial tension between the phases decreases, which contributes to the formation of a greater number of fine droplets and leads to more stabilized emulsion having a larger interfacial area within each unit (Nosrati et al. 2011); consequently, cyanide removal increases. However, when the Span-80 concentration reaches a certain level, any further increase in the surfactant concentration causes an increase in the membrane phase-internal phase interfacial viscosity. The increased interfacial viscosity augments the cyanide penetration resistance from the external phase to the emulsion phase, which subsequently decreases cyanide removal.

**Relationship of Span-80 content and NaOH content**

The contour plot in Figure 3(b) implies that there is a strong function of Span-80 and NaOH content in cyanide removal. At the lowest NaOH volume fraction (1.0%, coded value), the removal of total cyanide increases (to 93.34%) as the Span-80 content increases. Meanwhile, when the volume fraction of NaOH increases, total cyanide removal increases slowly. The extraction efficiency reaches a maximum value (79%) when the Span-80 and NaOH fractions are 2.5% and 3%, respectively.

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### Table 3 | ANOVA for response surface reduced quadratic model

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<th>Source</th>
<th>Sum of squares</th>
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<th>F-value</th>
<th>p-value</th>
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*Standard deviation was 6.71; mean was 72.57%; R² was 0.81; adjusted R² was 0.93; coefficient of variation was 8.54%; predicted R² was 0.84; adequate precision was 10.624.
Relationship of Span-80 content and the emulsion-to-external-phase volume ratio

Figure 3(c), 3(e) and 3(f) show that when the emulsion-to-external-phase volume ratio changes from 0.05 to 0.33, the cyanide extraction efficiency initially increases significantly, but slows and declines at a volume ratio of approximately 0.19. Theoretically, it is reasonable to keep this ratio at a high value to obtain high extraction efficiency (Wan & Zhang 2002). However, in practice, increases of the ratio means an increase in the amount of emulsion relative to the cyanide concentration in the feed phase. Consequently, the emulsion dispersed in the external phase tends to form bigger droplets, which decrease the effective surface area between the external phase and the emulsion phase. Lower surface area of emulsion droplets is disadvantageous to cyanide removal. Moreover, higher ratios would inevitably increase treatment costs.

Relationship of TOA content and NaOH content

The effect of carrier TOA and NaOH concentration on the extraction of cyanide is presented in Figure 3(d). Cyanide extraction marginally increased as the carrier concentration increased to 3%, but decreased as the carrier concentration continued to increase. This response may be attributed to the fact that an increase in the carrier concentration results in an increase in the viscosity of the emulsion phase, which in turn leads to larger globules and reduces the extent of transfer of cyanide from the feed phase to the stripping phase. The maximum cyanide removal (83%) was achieved when the carrier concentration was 3%.

Relationship of TOA content and the emulsion-to-external-phase volume ratio

TOA is an excellent extraction agent, there is a strong anti-acid capacity in the TOA-kerosene micro-emulsion system,
and TOA is an active carrier in the extraction reaction (Rajasimman & Sangeetha 2009). Therefore, TOA concentration directly affects the stability and efficiency of the extraction liquid membrane. However, an increase in TOA content above a certain concentration results in breakage of the liquid membrane due to decreased stability of the emulsion droplets (Wan & Zhang 2002). The removal of cyanide was found to increase as both the volume fraction of TOA and the emulsion-to-external-phase volume ratio increased, but removal then decreased, as shown in Figure 3(e).

**Relationship of NaOH content and the emulsion-to-external-phase volume ratio**

Figure 3(f) shows the effects of NaOH content and external phase volume ratio on cyanide removal. Cyanide removal decreases as the volume fraction of NaOH increases to 5%...
but tends to increase as the NaOH volume fraction continues to increase. This result may be due to the fact that because NaOH solution is the ELM continuous phase, an increase in NaOH content is also accompanied by an increase in the rate of cyanide transfer to the continuous phase; however, because the surface area of the membrane is constant, the removal rate of total cyanide is restricted even with increases in NaOH content to 3%. When NaOH content further increases in excess of 3%, the transfer rate of cyanide accelerates gradually, and the removal of total cyanide tends to increase.

**Optimal response of cyanide removal**

In Figure 3, the elliptical nature of the contours and bending degree of the axes show the interaction between individual variables in affecting cyanide removal. Figure 3 shows that the extraction of cyanide was affected by variables in the following order of effect: NaOH > Span-80 > the emulsion-to-external-phase volume ratio > TOA. **Table 5** shows the prediction framework for finding the optimal values for these variables that resulted in maximum cyanide removal. The RSM analysis identified that the optimal variable values were: volume fraction of Span-80, 4%; volume fraction of TOA, 4%; volume fraction of NaOH, 1%; and emulsion-to-external-phase volume ratio, 1:7.

**CONCLUSIONS**

In this research, the separation and recovery of cyanide from wastewater using the ELM method was studied by varying the values of various parameters to find the optimum values (Span-80 4.00%, TOA 4.00%, NaOH 1.00%, and emulsion-to-water ratio 0.27) that maximized cyanide removal. The experimental extraction efficiency under the optimum conditions was as high as 95.31%. The actual removal of cyanide and the removal predicted by optimizing the values of Span-80, TOA and other factors was in close agreement. Each single factor affected the total removal of cyanide in the following order of effect: NaOH > Span-80 > the emulsion-to-external-phase volume ratio > TOA.

The findings of this study show that cyanide can be extracted from an aqueous phase efficiently using ELM technology and that ELM treatment can be applied for the treatment of cyanide-containing wastewaters. The study results provide the theoretical basis for effectively solving the problem of cyanide wastewater discharged by a variety of industries. Furthermore, results indicate that RSM analysis is a viable technique by which to optimize the operating variables in ELM treatment because predicted cyanide removal and experimentally measured removal agree closely, with a little deviation.

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