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Recovery of ionized nanosilver by emulsion liquid membrane process and parameters optimization using response surface methodology

Raja Norimie Raja Sulaiman[a,b], Norasikin Othman[a,*], Nor Aishah Saidina Amin[b]

[a]*Faculty of Chemical Engineering, Department of Chemical Engineering, Centre of Lipids Engineering and Applied Research (CLEAR), Universiti Teknologi Malaysia UTM, Skudai Johor 81310, Malaysia, Tel. +607 5535561; Fax: +607 5581463; email: norasikin@cheme.utm.my (N. Othman)*
[b]*Faculty of Chemical Engineering, Department of Chemical Engineering, Chemical Reaction Engineering Group (CREG), Universiti Teknologi Malaysia UTM, Skudai Johor 81310, Malaysia*

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ABSTRACT

The discharge of silver ions from nanosilver-based product into the environment has raised the ecological and human health concern due to the toxicity of silver ion, particularly on the release behaviour of ionized nanosilver from the wastage. Therefore, recovery of ionized nanosilver is highly necessary. In this research, emulsion liquid membrane technique was employed for ionized nanosilver recovery from the domestic waste. The liquid membrane consists of kerosene, Span 80, Cyanex 302 and acidic thiourea as the diluent, surfactant, carrier and stripping agent, respectively. The emulsion stability was investigated at different surfactant concentrations, agitation and homogenizer speeds. Response surface methodology (RSM) was applied for the optimization of process variables including treat ratio, sulphuric acid (H_2SO_4) and thiourea concentration in the recovery process. The results showed that the most stable emulsion was observed at 3% w/v of surfactant, 10,000 and 150 rpm of homogenizer and agitation speed, respectively. The optimum conditions obtained for the recovery process using RSM were: treat ratio (0.256), H_2SO_4 concentration (0.75 M) and thiourea concentration (0.85 M). At the optimized condition, the maximum recovery of ionized nanosilver was 84.74%.

Keywords: Recovery; Emulsion liquid membrane; Stability; Response surface methodology

1. Introduction

The release behaviour of nanosilver from various products such as textiles, washing machines and facades has been reported by several researchers [1–4]. Some of the nanosilver was released into wash water in the form of silver ions, while some of them were still present in the form of nanoparticles. Two types of washing socks tested by Benn and Westerhoff [1] indicated that 70–90% of the released nanosilver had been characterized as ionic silver in water using silver ion selective electrode. This finding also claimed that the formation of ionic silver in the solution increased when nanosilver was subjected for long exposure in water, as nanosilver was slowly oxidized and dissolved as silver ion form. Besides, Water Environment Research Foundation found out that at some level, these silver ions can inhibit the growth of bacterial populations which is crucial for biological treatment

*Corresponding author.

process. The more particular concern is the potential impact of silver ions on the microbial community in the wastewater treatment processes, since inhibition and loss of bacteria are essential for chemical oxygen demand (COD) reduction and nitrogen removal [5]. The silver ions interact with other dissolved organic matter and lead to the toxicity problems which are detrimental to the aquatic organism life. The observation shows that exposure to 5 ppm concentration of silver ion from ionized nanosilver can increase the mortality and causes heart malformation in zebra fish [6]. United States Environment Protection Agency (USEPA) has prescribed that the maximum concentration of 3.2 ppb silver ion can be released in fresh water and 1.9 ppb in salt water, based on the acute toxicity of silver to macro invertebrates and fish. These standards are enforced through the issuance of discharge permits at the state level [7]. Several methods have been introduced for the extraction and recovery of silver ions but provide some limitations. For instance, ultrafiltration leads to the membrane fouling and decomplexation of silver ion, while electrodialysis involves high operating cost and energy consumption [8,9]. Besides, electrochemical method leads to the large capital investment and expensive electricity supply [10]. Solvent extraction has also been proposed by Sole et al. [11] to treat the silver ion. This method provides the extraction and stripping processes, but not in one single stage. Moreover, this method also uses a huge quantity of carrier compared to the liquid membrane technology.

Liquid membrane technology has been invented for the metal removal and recovery which are simple in operation, fast, requires less chemical consumption and can treat the metal ions even in the concentration less than 10 ppm [12]. Emulsion liquid membrane (ELM) technique is carried out for the removal of various heavy metal ions such as cobalt, nickel, chromium, alkali metal and organic compounds using different ELM formulation study [13–19]. This process provides high rates of mass transfer owing to a large surface area within the emulsion globules and internal droplets [20]. Despite these advantages, ELM struggles with the limitations of emulsion instability, which are swelling and breakage, thus reducing the overall efficiency of ELM process. Swelling occurs when water molecules from the external phase are transferred inside the internal phase, which then dilutes the solute and reduces the solute concentration. During breakage, the stripping agent and extracted solute is leaked into the external phase. The most stable emulsion has been obtained when there was neither swelling nor breakage or emulsion with minimum occurrence of swelling [21].

In order to perform the extraction and recovery, the process should be optimized using response surface methodology (RSM). RSM is an advanced tool for the optimization studies in various processes [22]. In addition, RSM is also a collection of mathematical and statistical techniques for modelling and analysis of the problems, where the response is influenced by several factors and the objective is to optimize the significant variables or parameters. Two mostly used response surface experimental designs are Central Composite design (CCD) and Box–Behnken design (BBD). In this research, BBD was used as a tool for optimization, because it provides several advantages over the CCD method. As an independent quadratic design, it does not contain any embedded factorial design, in which the treatment combinations are at the midpoints of edges of the design space and at the centre. The design is rotatable (or nearly rotatable) and requires three levels for each factor (−1, 0, 1). When the number of the variables is three or four, the total number for experimental runs is less than CCD. Meanwhile, CCD was not applied because several ranges proposed for design of experiment (DOE) are out of ranges. This will certainly affect the ELM process.

This research paper presents the stability of water in oil emulsion and the optimization of independent variables for the recovery of ionized nanosilver from wash water solution using RSM. The important variables considered in the stability study consist of surfactant concentrations, homogenizer and agitation speeds. Moreover, the significant independent variables such as effect of treat ratio, H_2SO_4 and thiourea concentration have been studied for the optimization of ionized nanosilver recovery.

2. Materials and methods

2.1. Materials and apparatus

Kerosene (78% purity), Cyanex 302 (85% purity), Span 80 (99% purity) and thiourea (99% purity) in sulphuric acid (98% purity) as the diluent, carrier, surfactant and stripping agent solution, respectively, were purchased from Sigma–Aldrich. Nanosilver in the range less than100 nm was procured from Nanomaterial Sdn Bhd located in Selangor, Malaysia. Wash water was taken from a laundry service. Nitric acid (65% purity) and sodium hydroxide (99% purity) solutions obtained from Merck were used to adjust the initial pH of the wash water solutions. The properties of wash water are shown in Table 1. All these reagents and solutions were directly used as received from the manufacturer. The apparatus used in the study such

Table 1
Anions and cations content in the wash water

Concentrations (ppm)	
Cations	
Na	9.918
K	1.540
Ca	1.583
Ag	4.829
Anions	
Cl	56.83
NO_3^-	3,893.47
SO_4^{2-}	103.64

as homogenizer Heidolph Silent Crusher M Emulsifier for emulsion preparation, portable smart pH metre 108 (Milwaukee Model) for pH measurement, high voltage coalescer for the emulsion demulsification and Perkin Elmer Flame Atomic Absorption Spectrometer (AAS) for the measurement of silver ion concentration.

2.2. Emulsion stability study

The emulsion was prepared by dissolving an equal amount of organic phase containing Cyanex 302 in kerosene with a stripping agent solution. The stability test of emulsion was conducted for different surfactant concentrations, homogenizer and agitation speeds. The aim of this experiment was to select the appropriate parameter conditions which provide the most stable ELM. Different concentrations of Span 80 in kerosene and 0.005 M Cyanex 302 were mixed with 1.0 M acidic thiourea using homogenizer at 10,000 rpm for 5 min. The white milky emulsion was dispersed into the wash water solution at the agitation speed of 150 rpm for 5 min. The experiment was carried out with one factor at a time, and the best condition was used for further experiment involving extraction and recovery study. The test was conducted at the room temperature (i.e. ± 26˚C). The swelling percentage was calculated using Eq. (1) as shown below:

$$\%\ \text{Swelling}, S = \frac{V_t - V_i}{V_i} \times 100\% \quad (1)$$

where V_t represents the volume of emulsion after extraction and V_i represents the volume of emulsion before the extraction.

2.3. Extraction and recovery process

An equal volume (5 mL) of stripping agent and organic liquid membrane containing Cyanex 302 in kerosene was homogenized at 12,000 rpm within 5 min to form the primary emulsion. The primary emulsion was then dispersed into a 250 mL beaker containing 30 mL of about 5 ppm wash water of the nanosilver solution as an external phase. The mixture of external and emulsion phase was agitated using a motor stirrer at 150 rpm for 5 min. Then, the mixture was separated by pouring the solution into the separation funnel for about half an hour for phase separation. The emulsion part from the upper layer was collected and demulsified using a high voltage demulsifier until the two layers were completely separated. The concentration of silver ion in the external and internal phase after phase separation was measured using atomic absorption spectrometry (AAS). The same procedure was repeated for different operating conditions. The recovery performance of ELM was calculated using Eq. (2) as shown below

$$\%\ \text{Recovery}, R = \frac{C_{int \times \text{TR}}}{C_{ext}} \times 100\% \quad (2)$$

where C_{int} represents the concentration of silver in internal phase, and C_{ext} represents the concentration of the initial silver in the external phase. TR is defined as the treat ratio (volume ratio of emulsion to the external phase).

2.4. Experimental design

For the recovery process, two level full factorial designs (2^3) was applied in this study using three important parameters which have significant effects on the recovery of ionized nanosilver such as treat ratio, sulphuric acid concentration and thiourea concentration. These independent variables were designated as x_1,x_2 and x_3 and were investigated at three different levels (low, medium and high), and they were denoted as (−1, 0, and +1), respectively, as tabulated in Table 2. The variables were coded according to Eq. (3):

$$x_i = \frac{X_i - X_0}{\Delta X_i} \quad (3)$$

where x_i, X_i and X_0 are defined as the coded value, uncoded value (real value) and centre point values of an independent variable, respectively, while ΔX_i is the

Table 2
Experimental range and levels for the independent variables

Independent variable	Range and levels		
	−1	0	1
H_2SO_4 concentration, X_1 (M)	0.5	1.0	1.5
Thiourea concentration, X_2 (M)	0.5	1.0	1.5
Treat ratio, X_3	0.14	0.20	0.33

step change value. The statistical design and data analysis were accomplished by using statistical software. The number of experiments was optimized by BBD in order to demonstrate the interaction between the operating variables and their influence on the recovery percentage. Consequently, there were 15 experiments required to investigate the parameters at three levels. The central point in the design was repeated three times for estimation of errors and curvature. The central values chosen for this experimental design were sulphuric acid concentration of 1.0 M, thiourea concentration of 1.0 M and treat ratio of 0.20 in the uncoded form. Batch experiments were conducted to describe the effects of H_2SO_4 concentration (x_1), thiourea concentration (x_2) and treat ratio (x_3) on the silver recovery efficiency. The percentage recovery of ionized nanosilver was the response variable. (DOE) is shown in Table 3 and statistical analysis of the responses was carried out using StatSoft Statistica software version 8.0. The mathematical modelling for the recovery of ionized nanosilver was fitted to the second-order polynomial model as given in Eq. (4):

$$Y_i = \beta_\circ + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 \quad (4)$$

where Y_i is the dependent variable (recovery percentage); x_1, x_2 and x_3 are the independent variables; β_0 is the regression coefficient at the centre point; β_1, β_2 and β_3 are the linear coefficients; β_{11}, β_{22} and β_{33} are quadratic coefficients and β_{12}, β_{13} and β_{23} are the second-order interaction coefficients. The equations were validated by statistical analysis called analysis of variance (ANOVA). The analysis evaluates the model and its parameters, along with the determination of the individual and interactive influences of the parameters on the recovery efficiency. Student's *t*-distribution and *p*-value were applied to associate the significant effects of the variables with the response, and F-value was fixed to check the validity of the predicted quadratic equation for the ionized nanosilver recovery yield. Model terms were selected or rejected based on the probability value with 95% confidence level. Eventually, response surface contour plots were generated in order to visualize the individual and interactive effects of independent variables.

Table 3
Box–Behnken design matrix along with predicted and experimental values of percentage recovery of ionized nanosilver

Run	X_1 H_2SO_4 concentration (M)		X_2 Thiourea concentration (M)		X_3 Treat ratio		Recovery (%)	
							Experimental	Predicted
1	0.5	−1	0.5	−1	0.20	0	65.08	67.49
2	1.5	1	0.5	−1	0.20	0	56.92	47.34
3	0.5	−1	1.5	1	0.20	0	36.08	45.66
4	1.5	1	1.5	1	0.20	0	31.16	28.75
5	0.5	−1	1	0	0.33	−1	87.90	79.16
6	1.5	1	1	0	0.33	−1	44.60	47.85
7	0.5	−1	1	0	0.14	1	47.81	44.57
8	1.5	1	1	0	0.14	1	30.07	38.82
9	1.0	0	0.5	−1	0.33	−1	63.00	69.34
10	1.0	0	1.5	1	0.33	−1	48.50	47.67
11	1.0	0	0.5	−1	0.14	1	45.23	46.07
12	1.0	0	1.5	1	0.14	1	33.65	27.32
13	1.0	0	1	0	0.20	0	79.94	78.83
14	1.0	0	1	0	0.20	0	78.55	78.83
15	1.0	0	1	0	0.20	0	77.60	78.83

Table 4
Analysis of variance (ANOVA) for quadratic model of recovery of ionized nanosilver

Source	Sum of square (SS)	Degree of freedom (Df)	Mean square (MS)	*F*-value (calculated)	*F*-tabulated ($\alpha = 0.05$)
Regression	4,899.38	9	544.38	7.99	>4.77
Residual	340.807	5	68.16		
Total	5,240.19	14			

The adequacy of the fitted model was validated by ANOVA using Fisher *F*-test. Table 4 exhibits the ANOVA to check the *F*-values by comparing with the tabulated *F*-value. The mean squares were obtained by dividing the sum of squares of each of both sources of variations, the model and the error variances, with their respective degree of freedom. *F*-value is the ratio of the mean square of regression to the mean square of the error (residual). Based on the results obtained, ANOVA of the regression model showed that the model was remarkably significant from the calculated *F*-value (7.99). The tabulated *F*-value was used at a high confidence level (95%) in order to obtain a good prediction model. The *F*-values were higher than the tabulated *F*-value ($F_{0.05,9,5}$) by rejecting the null hypothesis at significance level of 0.05. Null hypothesis means that all variables did not give significant outcome to the recovery yield.

The significance of the model parameters was assessed by evaluating *p*-value and *t*-value. p-values were used as a tool to check the significance of each coefficient, which in turn indicates the interaction between the variables. Greater magnitude of *t*-value and the smaller *p*-value indicates that the corresponding coefficient is more significant [23]. When the *p*-value is less than 0.05, the model term is significant, while the *p*-value greater than 0.1 indicates that the model term is insignificant.

3. Results and discussion

3.1. Wash water characterization

Table 1 shows all the ions found in wash water solutions. Based on Table 1, wash water contains sodium, calcium and potassium while the anions were chloride, nitrate and sulphate. Even though there were many ions in the wash water as an external phase, silver ion was targeted to be extracted and recovered in this process. This could be attributed to the carrier properties chosen in this process where previously Cyanex 302 had been developed as a carrier for some transition metals extraction like cadmium, copper, gold and lead [24–27]. The silver extraction using some commercial sulphur containing extractants like SFI-6R, MSP-8, Cyanex 302 and Cyanex 301 indicated that the carrier containing P = S and P(S)SH functional groups strongly extracted the silver in the whole range of hydrochloric acid, except for the very high concentration [28]. In addition, sulphur substitution could increase the acidity of the carriers, making them particularly suitable for the extraction of soft lewis acid metal ions such as Ag(I), Ni(II) and Zn(II) in accordance to the Hard Soft Acid Base (HSAB) principle.

3.2. Emulsion stability study

Fig. 1 exhibits the effect of varying agitation speed, homogenizer speed and surfactant concentration on the performance of emulsion stability. It was observed that the percentage of emulsion swelling increased from 15 to 50%, with increase in the agitation speed from 150 to 450 rpm. Basically, with increase in the agitation speeds, high number of smaller emulsion globules were produced. This condition provides the high interfacial area available for membrane-internal interface, thus increasing mass transfer of water molecules from external phase into the internal phase. Besides, an entrainment swelling also occurs, which is caused by the entrainment of the external phase into the internal phase due to the repeated coalescence and re-dispersion of emulsion globules during the dispersion operation, hence, causing an increase of the internal phase volume [29]. Thus, a mild agitation of 150 rpm has been chosen for the next experiment.

Besides, it was observed at low homogenizer speed of 7,000 rpm, the emulsion swelling increased up to 20%. This can be attributed to the low speed that provides larger internal droplets which are conducive for their coalescence, hence, leading to the membrane swelling and breakage. With further increase in the speed to 10,000 rpm, no swelling was observed. At this stage, the emulsion seems to be more stable due to the high number of smaller internal droplets produced. These droplets which tend to coalesce among

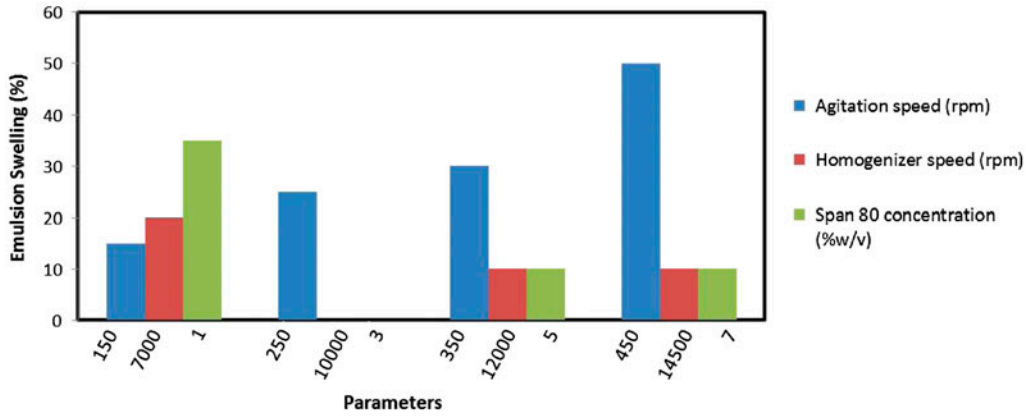

Fig. 1. Effect of agitation speed, homogenizer speed and surfactant concentration on the performance of emulsion swelling.

other droplets decrease the interfacial area available for mass transfer of water molecules inside the internal phase. Hence, this condition can prevent the heavy transportation of water molecules inside the internal phase. This finding has been strongly supported by Gasser et al. [30], who observed that the size of the internal phase droplets was smaller at high speed intensity, thus, producing more stable emulsion. Beyond 10,000 rpm, the swelling percentage increased gradually. It seems possible that this is due to smaller globules which coalesce among each other, hence causing their size to enlarge and leads to the breakage of membrane droplet. Besides, the swelling also took place among other globules at the same time. There exists a trade-off between these two effects. Hence, 10,000 rpm of homogenizer speed is highly preferable in producing the stable emulsion.

The effect of varying surfactant concentration on the performance of water in oil emulsion stability is depicted in Fig. 1. It could be seen that 35% of emulsion swelling was observed at low concentration of Span 80 (1% w/v). This is due to the insufficient surfactant to stabilize the emulsion, thus decreasing the emulsion stability. This finding is strongly supported by Dâas and Hamdaoui [31], who indicated that at low surfactant concentrations, the emulsion is not stable due to agglomeration of the internal droplets, whereas at high surfactant concentrations, the

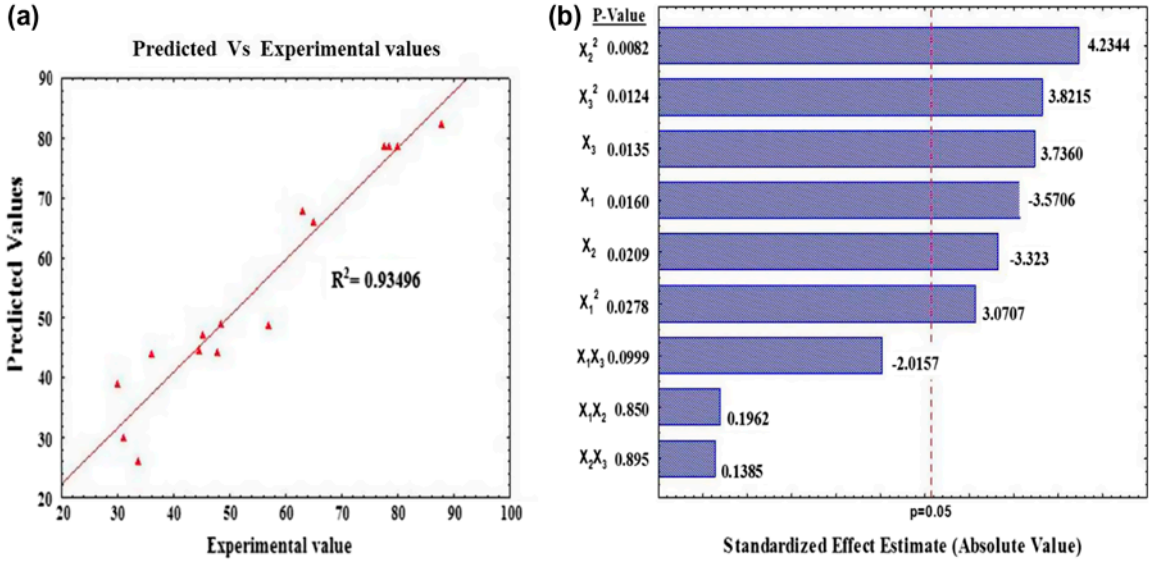

Fig. 2. (a) Predicted vs. experimental values for recovery percentage and (b) Pareto chart of each parameter coefficient for recovery yield.

emulsion destabilization occurs as a result of rapid coalescence. Basically, the number and size of internal droplets in the emulsion are influenced by the amount of surfactant used. With further increase in the surfactant concentration up to 3% w/v, emulsion swelling decreased to 10%. This can be explained by the fact that the higher surfactant concentration significantly reduces the interfacial tension which decreases the size of high number of internal droplets hence, enhancing the emulsion stability. This is in agreement with Malik et al. [32], who observed that the interfacial tension is a surface free energy which exists between two immiscible liquid phases, such as oil and water. The energy barrier produced by the interfacial tension prevents the formation of emulsion. Therefore, by adding the surfactant, the interfacial tension should be lowered. Beyond 3% w/v, the swelling percentage increased gradually. This can be attributed that the higher concentration of Span 80 can help the transportation of water molecules inside the internal phase. Thus, 3% w/v Span 80 concentration is adequate for the subsequent experiment.

3.3. Model analysis

The effect of process variables such as treat ratio, sulphuric acid concentration and thiourea concentration on the recovery percentage of silver ion was investigated using RSM according to BBD design. The batch run was conducted according to the BBD designed experiment to visualise the effects of independent variables on the response. The second-order polynomial model for the percentage recovery of silver is illustrated as in Eq. (5):

$$Y = -179.35 + 120.65x_1 + 119.56x_2 + 1292.56x_3 - 52.77x_1^2 - 72.77x_2^2 - 2170x_3^2 + 3.24x_1x_2 - 169.52x_1x_3 + 11.65x_2x_3 \quad (5)$$

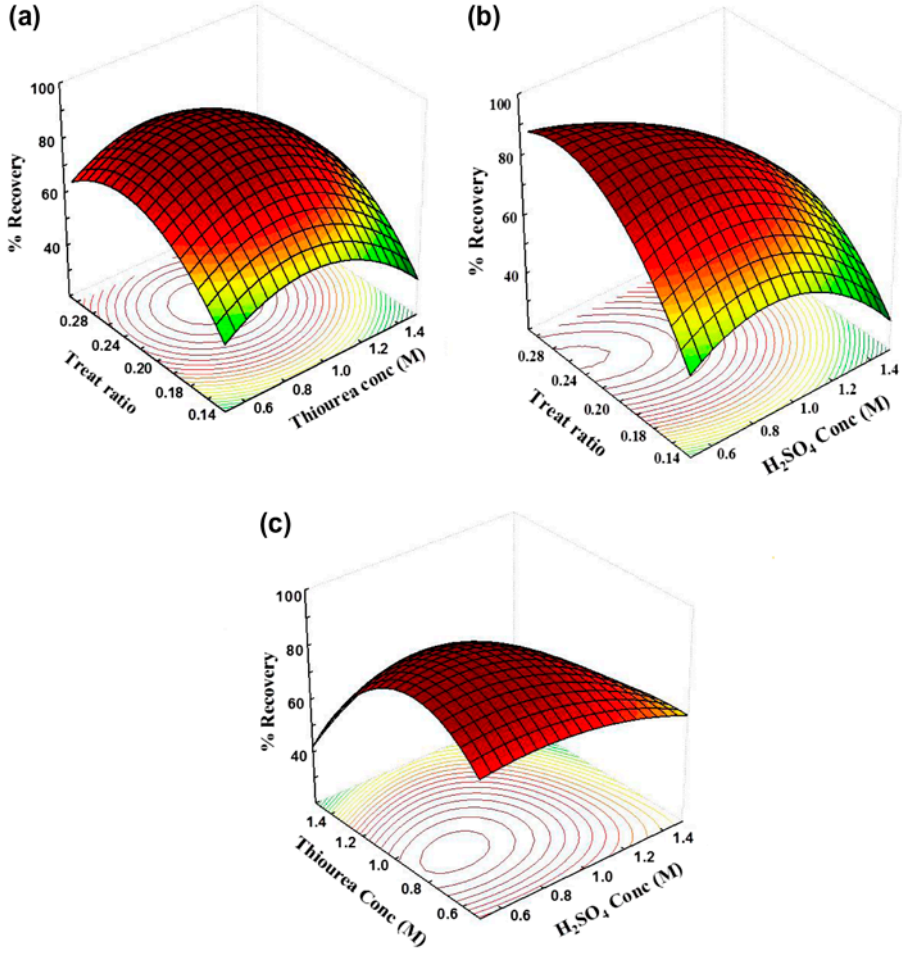

Fig. 3. 3D response surface plots of recovery of ionized nanosilver: (a) the effect of thiourea concentration and treat ratio, (b) the effect of H_2SO_4 concentration and treat ratio, and (c) the effect of H_2SO_4 concentration and thiourea concentration.

where Y is the percentage recovery, x_1 is H_2SO_4 concentration, x_2 is thiourea concentration and x_3 is the treat ratio. The predicted percentage recovery of silver is plotted against the experimental value as demonstrated in Fig. 2(a). The value of the regression coefficient ($R^2 = 0.\ 93496$) was closer to 1, which indicates that the correlation is fit or best suited in predicting the values of the recovery system, and the predicted values were found to be closer to the experimental results. The high value of R^2 value can clarify that the model obtained was able to convince a good estimate of the response within the process conditions range [33]. The data points on a graph of the actual response values versus the predicted response values should be split evenly and close to the 45 degree line, which means that there is a good agreement between the predicted and experimental values [34].

Fig. 2(b) shows the Pareto chart which exhibits the significance of variables with p-value and t-value. It could be revealed that the linear effect of H_2SO_4 concentration ($p = 0.0160$), thiourea concentration ($p = 0.0209$) and treat ratio ($p = 0.0135$) were more significant. Moreover, the quadratic effects of H_2SO_4 concentration ($p = 0.0278$), thiourea concentration ($p = 0.0082$) and treat ratio ($p = 0.0124$) also possessed remarkable effects on the recovery percentage of ionized nanosilver using an ELM. The Pareto chart also showed that the effect of thiourea concentration was the most significant factor in the efficiency of silver recovery.

3.3.1. Effect of variables on the response

In order to get an excellent understanding on the effects of independent variables and their interactions with the dependent variables, three-dimensional (3D) response surface plots of the measured responses were produced based on the model equation. The relationship between the dependent and independent variables was further elucidated by constructing surface plots as shown in Fig. 3. The interaction effects were considered within the variable range. A circular contour implies that the interaction between the variables is not significant, whereas an eclipse contour implies there is an interaction among the variables [23].

Fig. 3(a) and (b) shows the effect of treat ratio on the ionized nanosilver recovery efficiency. The treat ratio was varied by changing the amount of aqueous feed phase and keeping the volume of the emulsion constant. The treat ratio also controlled the interfacial mass transfer across an ELM. It can be observed that the recovery efficiency increased significantly with the increase in the treat ratio from 0.14 to 0.33. Basically, high treat ratio significantly increased the emulsion phase hold up in the feed phase, which then simultaneously increased the extraction and recovery capacity. This finding is supported by Jiao et al. [35], who observed that the high treat ratio increases the amount of emulsion required for the feed phase to be treated. In contrast, at low treat ratio, the emulsion phase did not disperse very well and the contact area between both phases decreased significantly. In addition, emulsion phase tends to swell or break, hence diluting the silver concentration in the stripping phase which decreased the specific surface area between both emulsion and feed phase, and it is not good for the extraction and recovery efficiency.

Fig. 3(a) and (c) demonstrates 3D response contour plots effect of thiourea concentration on the recovery performance. It was observed that when the concentration in the internal phase exceeds 1.0 M, the recovery efficiency showed a downward trend. Basically, thiourea can act as a co-carrier and form complexes with silver ion in the membrane-internal interface. At low thiourea concentrations, there was insufficient amount of thiourea to strip the silver into the internal phase. In contrast, an increment in thiourea concentration up to certain amount also increased the recovery yield. This condition helps the silver ions to be stripped into the internal phase, hence enhancing the recovery efficiency. Further increase in thiourea concentration gradually decreased the recovery percentage. This can be attributed to the salt formation which leads to the emulsion breakage. This condition destabilizes the emulsion and leads to the recovery inefficiency [36].

Table 5
Comparison condition between the experimental and RSM optimization

Conditions	Experimental optimization	RSM optimization
Thiourea concentration (M)	1.5	0.85
Sulphuric acid concentration (M)	1.5	0.75
Treat ratio	0.33	0.256
Recovery (%)	100	84.74

Table 6
Predicted analysis of optimum condition for recovery percentage

Variables	Observed minimum	Critical values	Observed maximum
H_2SO_4 concentration	0.05 M	0.75 M	1.5 M
Thiourea concentration	0.05 M	0.85 M	1.5 M
Treat ratio	0.14	0.256	0.33

Table 7
Comparison between the predicted and the experimental (observed) response at the optimum condition from RSM

Response	Observed value	Predicted value	Error (%)
Recovery (%)	84.74	85.61	1.01

The effect of H_2SO_4 concentration on the ionized nanosilver recovery efficiency is exhibited in Fig. 3(b) and (c). It was observed that the recovery yield increased up to 1.0 M and decreased thereafter. This is due to the fact that the augment of H_2SO_4 concentration significantly increased the concentration of hydrogen ion in the stripping phase, therefore enhancing the ionic strength of stripping phase. This condition induces the transportation of the solute from external phase into the internal phase [37,38]. Nevertheless, further increase in H_2SO_4 concentration only increased the swelling percentage significantly. This can be explained by the fact that the osmotic pressure gradient between both phases allows the transportation of more water molecules from the external phase into the stripping phase. This finding is in agreement with Teresa et al. [39], who found that the differences of ionic strength between the two aqueous phases can promote the transfer of water molecules from the feed phase into the internal phase and decrease the recovery efficiency.

3.3.2. Optimization of ionized nanosilver recovery

The optimization using conventional step was conducted on the standard aqueous silver solution where the optimum condition for 100% recovery of silver ions are 1.5 M H_2SO_4 concentration, 1.5 M thiourea concentration and treat ratio of 0.33. After that, the ranges obtained from the conventional step were used for the optimization using BBD. The optimum conditions of the operating variables lies within the range of 0.75 M H_2SO_4 concentration, 0.85 M thiourea concentration and treat ratio of 0.256 for the prediction of high ionized nanosilver recovery efficiency. The comparison for both conventional and RSM optimization were tabulated in Table 5.

For RSM optimization, further analysis by experimental was performed using the optimum conditions from Table 6. The result shows that 84.74% of ionized nanosilver was recovered compared to the predicted result, where only 1.01% error was found between the experimental and the predicted values as shown in Table 7.

4. Conclusions

In this work, the effect of surfactant concentration, homogenizer and agitation speed showed significant and positive influence on the water in oil emulsion stability. The most stable emulsion was observed at 3% w/v of Span 80 concentration, 10,000 rpm and 150 rpm of homogenizer and agitation speed, respectively. Statistical BBD and RSM were able to demonstrate the important influence of three independent variables studied which are treat ratio, H_2SO_4 concentration and thiourea concentration. An empirical relationship between the response and the independent variables was achieved. ANOVA showed a high R^2 value of regression model equation ($R^2 = 0.93496$), which ensures a sufficient adjustment of the model with the experimental data. In addition, it was found that the linear and quadratic effects of treat ratio, H_2SO_4 concentration and thiourea concentration have significant influence on the efficiency of silver recovery. The optimum conditions for the recovery of ionized nanosilver using RSM were treat ratio (0.256), H_2SO_4 concentration (0.75 M) and thiourea concentration (0.85 M). At the optimized condition, the maximum recovery of ionized nanosilver was found to be 84.74%.

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