Aqueous two-phase extraction of lead from contaminated aqueous solutions

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Abstract. Aqueous two-phase extraction is an ecologically safe method for heavy metal recovery and regeneration from contaminated aqueous solutions. Investigation has been carried out experimentally for the extraction of lead from aqueous solutions using Polyethylene Glycol 1500- Ammonium sulfate two-phase system. The extracting agent used is sodium chloride. Aqueous two-phase extraction experiments for Pb(II) have been performed in batch mode according to the central composite design under Response Surface Methodology. The effect of independent parameters as to the extractant concentration, initial salt solution pH, and initial salt phase metal concentration on the extraction efficiency has been studied experimentally. The results indicate that all the three independent parameters studied have significant effect on extraction efficiency. A second-order polynomial model has been used to fit the dependent variable in the experimental range of parameters. The maximum extraction efficiency obtained from the model is about 51% at initial salt solution pH of 2.8, NaCl concentration of 49.9 mmol/L and initial salt phase lead concentration of 9.8 mg/L. This is in agreement with the results obtained from the experiment conducted at optimum conditions.

1. Introduction

Lead is a naturally occurring metal and its resources are limited. This heavy metal is widely used in our day to day life as lead-acid batteries, pigments, ceramics, cosmetics, and many more. Lead is one of the 10 Chemicals identified by the World Health Organization causing concern to the public health. Considering the importance of the issue, the International Lead Poisoning Prevention Week is observed every year since 2013 by the organization. Lead is a potent neurotoxin affecting children under the age of five. Lead regeneration is vital from the environment and economic point of view.

Solvent Extraction is a widely used technique for metal regeneration. Its advantages over other techniques include fast kinetics, scalability, sludge free process, etc. Disadvantages include the use of organic solvents which are toxic, flammable, volatile, and expensive. Aqueous two-phase extraction (ATPE) overcomes the listed disadvantages of solvent extraction. Polymer/salt systems, polymer/salt systems, salt/salt systems, and ionic liquids/salt systems are commonly used for ATPE. Polymer salt systems are more cost-effective compared to other systems. Polyethylene Glycols with molecular weight (1200-6000) have gained ample attention in ATPE of metal ions due to their biocompatibility, low cost and low volatility [1].
In the present work PolyEthylene Glycol with average molecular weight 1500 (PEG 1500) is used as the polymer. PEG 1500 is widely used in the pharmaceutical industry, wood industry, cosmetics, and chemical industry. Lead is a soft metal that can be extracted with halide ions to the PEG phase[1]. Sodium chloride is selected as the extracting agent due to its low cost and commercial availability. Ammonium sulfate is a low cost commercially available chemical and can be precipitated by adding methanol and recycled. PEG – (NH$_4$)$_2$SO$_4$ aqueous two-phase system has been extensively studied for the extraction of metals as it satisfies the conditions of green chemistry [2-11]. With 40% (w/w) PEG 1500 and 40% (w/w) ammonium sulfate, phase separation can be rapidly obtained and the interface between the two phases is distinct [2, 4-11]. However, studies on the optimization of the independent parameters using the central composite design (CCD)and the validation using experimental analysis have been found to be sparse in the literature. The present study aims at optimizing the independent parameters for the extraction of lead using the 40% PEG- 40% (NH$_4$)$_2$SO$_4$ two-phase system with NaCl as extractant. The effect of the independent parameters as to the extractant concentration, initial pH of salt solution, and initial salt phase metal concentration on the extraction efficiency has been studied experimentally. The extraction efficiency at the optimum conditions is compared with model prediction using RSM studies. The central composite design (CCD) is employed and the optimum conditions are reported.

2. Materials and methods
Polyethylene glycol (Molecular Weight 1500, LobaChemie Pvt.Ltd. (Mumbai, India)), Sodium chloride (Isochem laboratories (Kochi, India)), lead nitrate nonahydrate (Sigma- Aldrich) and Ammonium sulfate (Merck Life Science Pvt. Ltd, Mumbai, India) have been used for the experiments. All the chemicals were used without further purification. Millipore water has been used throughout the experiment.

The analysis is performed using Atomic Absorption Spectrophotometer (Thermo Scientific Ice 3000 series). 0.1 N, H$_2$SO$_4$, and NaOH have been used for pH adjustments. pH meter (Eutech instruments pH Tutor) has been used for the pH measurements during experiments.

3. Experimental procedure
A stock solution of Pb(II) with a concentration of 1000 mg/L is prepared by dissolving lead nitrate in Millipore water which is subsequently diluted to the required concentrations and used for the experiments. The required quantity of solid PEG (Average molecular weight 1500 g/mol) is dissolved in distilled water to prepare PEG solution. Predetermined quantity of (NH$_4$)$_2$SO$_4$ dissolved in Millipore water has been used to prepare the salt solution. Sodium chloride solution (1 mol/L) is prepared and further diluted as per requirement.

3.1. Extraction protocol
The batch mode extraction experiments have been performed at room temperature. Each extraction system is prepared by mixing 4ml of pH adjusted 40% (w/w) salt with 1 ml of extractant NaCl and 1 ml of known concentration of lead nitrate solution to get the salt solution of the desired metal concentration. 4ml of 40% (w/w) PEG solution is subsequently added to the above solution. The contents have been vigorously shaken for 10 min and centrifuged for the same duration at 1500 rpm. Each phase has been carefully separated with a Pasteur pipette and 1ml of the solution is taken, diluted, and analyzed for the lead concentration.

3.2. Experiment design and optimization using RSM
Three independent variables that influence the efficiency of extraction have been identified from literature and preliminary experiments conducted. The present study used initial salt solution pH, initial concentration of metal ion in the salt phase and NaCl concentration as the variables. The preliminary experiments have been conducted for a selected range of parameters. The ranges of variables selected include the initial salt solution pH of 3-8, metal ion concentration of 2-60 ppm in the salt phase and NaCl concentration of 0.02- 0.1 mol/L.
The optimization of the parameters has been done using Response Surface Methodology (RSM) which is a set of mathematical and statistical techniques[13]. Optimization studies were performed in the present study using Minitab statistical software version 16. The effect of the selected independent parameters such as the extractant concentration, initial salt solution pH, and the initial salt phase metal concentration on the extraction efficiency has been examined by employing the Central Composite Design (CCD). Operating ranges of the optimization experiments have been selected from the results obtained from preliminary experiments. CCD with three factors at 5 levels has been applied in the optimization analysis. Table 1 provides the operating parameters and their ranges used in the experiments. Twenty experiments were conducted including six replicates at the center point. Experiments were done in triplicate to reduce variability in data collection and the average efficiency has been calculated as below.

The extraction efficiency (E) is given by the equation,

\[
\%E = \frac{\text{mass of lead extracted to the top phase}}{\text{mass of lead in both phases}} \times 100
\]

(1)

Table 1. Independent variables and their levels used for central composite design

| Independent variables | Coded level (α = 1.2) |
|-----------------------|-----------------------|
|                       | -∞   | -1    | 0    | +1    | +∞   |
| Salt stock solution pH| 2.8  | 3     | 4    | 5     | 5.2  |
| Initial metal ion concentration (aquaeous phase(ppm)) | 0.2  | 2     | 11   | 20    | 21.8 |
| NaCl concentration (mol/L) | 0.016 | 0.02  | 0.04 | 0.06  | 0.064 |

Analysis is carried out using RSM and the efficiency is found out from the experiments. Experimental data have been fitted using a second-order polynomial of the following form.

\[
Y = C_0 + C_1X_1 + C_2X_2 + C_3X_3 + C_{11}X_1^2 + C_{22}X_2^2 + C_{33}X_3^2 + C_{12}X_1X_2 + C_{13}X_1X_3 + C_{23}X_2X_3
\]

(2)

Here Y is the extraction efficiency (%); \(C_0\) is a constant; \(C_1, C_2, C_3\) are the regression coefficients representing the linear effects; \(C_{11}, C_{22}, C_{33}\) are quadratic coefficients; \(C_{12}, C_{13}, \) and \(C_{23}\) are the interaction coefficients. The extraction efficiency (%) for different combinations of three independent variables within the experimental ranges performed has been obtained from model prediction. RSM has been used to perform the Analysis of variance (ANOVA). The optimal sets of parameters that maximize extraction efficiency have been determined.

4. Results and discussions

The effectiveness of PEG 1500 -ammonium sulfate aqueous two-phase system with NaCl as an extracting agent for the extraction of lead is studied experimentally and optimized using RSM studies.

4.1. Preliminary experiments

4.1.1. Effect of NaCl concentration on extraction efficiency: The effect of the extracting agent on the extraction of lead has been investigated over a range of independent parameters. The NaCl concentration used in the experiments ranges from 0.02 mol/L to 0.1 mol/L for a constant pH 3 and metal concentration at 10 ppm. Maximum efficiency of 43% is obtained at 0.04 mol/L. From the present experimental investigation, it has been observed that the extraction efficiency reached a maximum at 0.04 mol/L chloride ions and indicated to fall off for all other tested chloride ion levels. This decrease in efficiency at higher chloride ion concentration may be due to the formation of unstable hydrophilic lead chloride anionic complexes. The findings reported by the investigators for the extraction of zinc using ATPS are also in tune with the observation made in the present study[2].
4.1.2. Effect of salt solution pH on extraction efficiency. The salt stock solution pH is an important parameter that determines the speciation of metal ions between the two phases. The pH of the salt stock solution is varied from 3-8 by keeping the extracting agent concentration at 0.04 mol/L and initial metal concentration in the salt phase at 10 ppm. Maximum efficiency is obtained at a pH of 3. At low pH, the dehydration of the PEG phase occurs and the extraction efficiency gets enhanced for most of the metal ions. Similar results were reported by other researchers also [2, 11, 12, 14].

4.1.3. Effect of metal ion concentration on extraction efficiency. Pb(II) concentration in the salt phase has been varied from 2 ppm - 60 ppm with NaCl concentration 0.04 mol/L and salt solution pH 3. Maximum extraction efficiency is observed at 10ppm. At low concentrations, the extraction efficiency is found to be increasing with metal concentration up to 10 ppm, and thereafter a reduction in extraction efficiency is observed with further increase in the metal concentration. The decrease in efficiency is attributed to the overloading of PEG phase with the metal ions. Similar results have been reported for the extraction of Zn (II) ions in the initial concentration range 30 to 65 g/mL using PEG-1550/ (NH₄)₂SO₄ ATPS. It has been further reported that the extraction efficiency of Zn(II) ions increased up to 55 ppm with the increase in initial concentration and got decreased thereafter in the presence of 0.05 M chloride ions[2]. Similar observations have been reported for the extraction of Cu(II) ions using the PEG 2000-sodium sulfate system wherein the extraction efficiency increased up to 7 ppm and then got decreased [12].

4.2. Optimization using RSM
Experimental results on the metal ion extraction efficiency (%) in the various ranges of the independent parameters obtained from the 20 runs as demanded by the CCD of RSM are tabulated in table 2.

### Table 2. Experimental data and results of CCD

| Sl. No. | NaCl concentration, mol/L | Initial salt solution pH | Initial salt phase concentration of Pb(II), ppm | Efficiency (%) |
|---------|---------------------------|--------------------------|-----------------------------------------------|----------------|
| 1       | 0.04                      | 5.2                      | 11                                            | 36.32          |
| 2       | 0.04                      | 4                        | 11                                            | 40.55          |
| 3       | 0.06                      | 3                        | 20                                            | 30.03          |
| 4       | 0.04                      | 4                        | 11                                            | 42.21          |
| 5       | 0.02                      | 3                        | 20                                            | 35.99          |
| 6       | 0.04                      | 4                        | 11                                            | 40.87          |
| 7       | 0.02                      | 5                        | 20                                            | 29.37          |
| 8       | 0.06                      | 5                        | 2                                             | 20.58          |
| 9       | 0.064                     | 4                        | 11                                            | 42.63          |
| 10      | 0.04                      | 4                        | 21.8                                          | 26.01          |
| 11      | 0.02                      | 5                        | 2                                             | 10.99          |
| 12      | 0.04                      | 4                        | 11                                            | 37.78          |
| 13      | 0.04                      | 4                        | 11                                            | 40.66          |
| 14      | 0.04                      | 4                        | 0.2                                           | 22.66          |
| 15      | 0.016                     | 4                        | 11                                            | 31.08          |
| 16      | 0.06                      | 5                        | 20                                            | 30.22          |
| 17      | 0.04                      | 4                        | 11                                            | 44.15          |
| 18      | 0.06                      | 3                        | 2                                             | 40.26          |
| 19      | 0.02                      | 3                        | 2                                             | 26.01          |
| 20      | 0.04                      | 2.8                      | 11                                            | 51.85          |
ANOVA of the % extraction efficiency is given in Table 3. Based on the sum of squares, the importance of the independent variables on the extraction of Pb ions can be ranked in the following order: pH of salt solution ($X_1$) > extractant concentration ($X_2$) > initial metal ion concentration in the salt phase ($X_3$). The P-test is used to analyze the significance of the regression coefficients. The values of $P$ obtained is given in Table 3, indicating the significant influence of all the independent parameters on the efficiency of extraction. The F-value of 29.5 for regression which is higher than the given value of 3.02 in the standard statistical table shows that the model fits well for the design space.

**Table 3. ANOVA results**

| Source          | DF | Sum of Squares | Mean Squares | F    | P     | Significance level, (1-P)% |
|-----------------|----|----------------|--------------|------|-------|---------------------------|
| Model           | 9  | 1721.69        | 191.299      | 29.5 | <0.001| > 99                      |
| Linear          | 3  | 518.75         | 91.912       | 14.17| 0.001 | > 99                      |
| $X_1$           | 1  | 328.19         | 48.612       | 7.5  | 0.021 | > 97                      |
| $X_2$           | 1  | 97.68          | 67.118       | 10.35| 0.009 | > 99                      |
| $X_3$           | 1  | 92.88          | 166.804      | 25.72| <0.001| > 99                      |
| Square          | 3  | 997.61         | 332.535      | 51.28| <0.001| > 99                      |
| $X_1^2$         | 1  | 61.85          | 18.005       | 2.78 | 0.127 | > 87                      |
| $X_2^2$         | 1  | 207.52         | 51.657       | 7.97 | 0.018 | > 98                      |
| $X_3^2$         | 1  | 728.24         | 728.244      | 112.31| <0.001| > 99                      |
| Interaction     | 3  | 205.33         | 68.445       | 10.56| 0.002 | > 99                      |
| $X_1$*$X_2$     | 1  | 0.57           | 0.573        | 0.09 | 0.772 | > 22                      |
| $X_1$*$X_3$     | 1  | 99.94          | 99.938       | 15.41| 0.003 | > 99                      |
| $X_2$*$X_3$     | 1  | 104.82         | 104.82       | 16.17| 0.002 | > 99                      |
| Residual Error  | 10 | 64.84          | 6.484        |      |       |                           |
| Lack of fit     | 5  | 42.74          | 8.548        | 1.93 | 0.243 | >0.05                     |
| Pure error      | 5  | 22.1           | 4.421        |      |       |                           |

Table 3 gives the regression analysis of the data in uncoded units and the fitted model obtained is given by the following quadratic equation (3):

$$Y = 63.63 - 25.25X_1 + 948.7X_2 + 2.78X_3 + 1.86X_1^2 - 7890.29X_2^2 - 0.15X_3^2 + 13.39X_1X_2 + 0.39X_1X_3 - 20.11X_2X_3$$

(3)
Here $Y$ is the extraction efficiency (%) in uncoded units and $X_1, X_2, X_3$ represents initial salt solution pH, extractant concentration, and initial metal ion concentration in the salt phase.

The model exhibits a high determination coefficient ($R^2 = 0.9637$) and the adjusted determination coefficient ($R^2 (adj) = 0.931$), suggesting the high significance of the model.

The response is optimized using the predicted model and is plotted in Figure 1. The optimum efficiency of 51.18 % is predicted. The optimum conditions predicted are initial salt solution pH of 2.8, NaCl concentration of 49.9 mmol/L, and initial salt solution metal concentration 9.8 mg/L. Experiments were conducted at optimized conditions and average efficiency of 50.68 % is observed.

**Figure 1.** Optimization plot

Figure 2 gives the comparison of the experimental value of extraction efficiency of lead at different experimental conditions used in the study with the values predicted by the quadratic model obtained which shows good agreement between the two. Contour plots of various parameters are plotted in Figure 3.

**Figure 2.** Comparison of experimental and predicted values
5. Conclusions

The extraction of Pb(II) using aqueous 40% PEG 1500 - 40% \((\text{NH}_4)_2\text{SO}_4\) two-phase system is investigated experimentally and optimized as a function of the independent variables of concentration of chloride ions, initial pH of salt solution, and initial concentration of Pb(II) in the salt phase. While varying the initial concentration of Pb(II) in the salt solution, a peak in the extraction efficiency is observed. For further higher values of the initial metal ion concentrations, the extraction efficiency has been found to decrease, which could be due to the overloading of PEG phase with the metal ion. Similarly decrease in extraction efficiency is observed at higher concentration of chloride ions. This decrease in efficiency is attributed to the formation of lead chloride anionic complexes. The low pH of salt solution favored the dehydration of the PEG phase and the extraction efficiency gets enhanced.

The optimum values of the independent variables affecting the extraction were determined using Response Surface Methodology. Central composite design under Minitab statistical software version 16 has been used for modeling the extraction process. The optimum extraction efficiency of nearly 51% has been predicted for a chloride ion concentration of 49.9 mmol/L, salt solution pH of 2.8, and an initial metal ion concentration of 9.8 ppm which is in agreement with the experimentally obtained efficiency. The studied system satisfies the conditions of sustainability as the extraction of lead from highly contaminated aqueous solutions can be performed using a green solvent.
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