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# Optimization studies on aqueous two-phase extraction of hexavalent chromium from contaminated aqueous solutions

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**Abstract.** Chromium has wide applications in industry and its resources are limited. The total chromium discharge to the environment needs to be monitored and regulated. The extraction of chromium to PEG offers its reuse in pure form. The present study focuses on the optimization of hexavalent chromium extraction to PEG 1500 using ammonium salt. The effect of independent parameters as to the initial salt solution pH and initial salt phase metal concentration on the extraction efficiency has been studied experimentally. Second-order polynomial models have been used to fit the dependent variables in the experimental range of parameters. Central composite rotatable design in Minitab statistical software version 16 is used as the optimization tool. The maximum efficiency that is achieved through the optimization studies is 29.8% at an initial salt solution pH of 6.5 and initial metal concentration 24.4 ppm. The corresponding distribution coefficient at the optimum conditions has been found to be 1.14. The results of the optimization studies have been validated by conducting experiments at the optimum conditions.

## 1. Introduction

Heavy metal contaminated solutions impose a severe threat to the environment due to their bioaccumulation capability. Extraction and recycling of these metals from contaminated aqueous solutions is a significant step in sustainable development. Various technologies such as adsorption, chemical precipitation, membrane separation, ion exchange, liquid-liquid extraction, and electrocoagulation are widely accepted methods for heavy metal removal from aqueous solutions. These techniques have inherent advantages and disadvantages. Aqueous two-phase extraction (ATPE) emerged as a green alternative to the liquid-liquid extraction method. Compared to liquid-liquid extraction ATPE is an environmentally benign method it contains only water-soluble biocompatible components [1].

Chromium is extensively used in industries and its usage in our day to day life is unavoidable. In nature, chromium exists in every oxidation state from 2 to 6. However, only three forms - zero, trivalent, and hexavalent chromium is used in industries. Trivalent and hexavalent chromium are more stable compared to other forms. Hexavalent chromium is a well established anthropogenic carcinogen. Major consumers of chromium include the tanning industry, wood preservation, electroplating, and pigment industry [2]. The maximum concentration of wastewater discharge permitted by CPCB India



for total chromium is 2 ppm and for hexavalent chromium, it is 1ppm for marine coastal areas, for inland water discharge it is only 0.1 ppm [3].

Aqueous two-phase extraction of metals using PolyEthylene Glycol (PEG) and salt solutions has been studied by numerous researchers [4]. PEG is considered a green reaction media; it is stable and has a high boiling point. In the present study, PEG 1500 and ammonium sulfate are used as they are low cost and commercially available. With 40% (w/w) each for PEG 1500 and ammonium sulfate, phase separation can be rapidly obtained and the interface between the two phases is clear [5-13]. Metal ion extraction in the aqueous two-phase system (ATPS) can be achieved through three routes. In one method inorganic ions such as halide and thiocyanate ions are used as extracting agents. The second method uses chelating agents that aid in the partition. Chromium(VI) extraction belongs to the third group in which direct extraction of the metal ions to the PEG rich phase is possible [4].

In the present study the efficiency of Cr(VI) extraction is studied by varying two significant extraction parameters, initial salt solution pH and metal ion concentration, in PEG 1500 -ammonium sulfate system by maintaining a constant temperature. The optimization is carried out by response surface methodology (RSM) using central composite rotatable design in MINITAB statistical software version 16.

## 2. Materials and methods

Polyethylene glycol (Molecular Weight 1500), Potassium dichromate and Ammonium sulfate have been obtained from LobaChemie Pvt. Ltd. (Mumbai, India), Sigma Aldrich and Merck life science Pvt. Ltd. (Mumbai, India) respectively. The above chemicals have been used for experiments without further purification. Millipore water is used throughout the experiment.

The analysis is performed using Atomic Absorption Spectrophotometer (Thermo Scientific iCE3000 series). pH adjustments have been made using 0.1 N, H<sub>2</sub>SO<sub>4</sub> and NaOH. pH meter (Eutechinstruments pH Tutor) has been used for the pH measurements during experiments.

## 3. Experimental procedure

Cr(VI) stock solution (1,000 mg/l) is prepared by dissolving potassium dichromate in Millipore water and the solution is further diluted for getting various concentrations. PEG solution is prepared by dissolving a suitable quantity of solid PEG with an average molecular weight of 1500 g/mol in distilled water. The salt solution is prepared by dissolving a suitable quantity of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> in Millipore water.

### 3.1. Extraction protocol

The batch mode extraction experiments have been performed at room temperature. Each extraction system has been prepared by mixing 5ml of pH adjusted 40% (w/w) salt with 1 ml of known concentration of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution to get salt solution of the desired metal concentration. 4 ml 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 total chromium concentration.

### 3.2. Experiment design and optimization using RSM

Literature studies reveal that metal concentration and initial salt solution pH has a significant effect on metal ion removal efficiency [4-14]. The chromium concentration in most of the industrial effluents is in the range 10-120 ppm and the pH is in the range 3-8 [15-18]. The preliminary experiments have been conducted for a selected range of parameters. The ranges of variables selected include the initial salt solution pH of 3-7 and metal ion concentration 10-80 ppm. The maximum efficiency obtained is 26% at an initial salt phase metal ion concentration of 20 ppm and an initial salt solution pH of 6. Maximum efficiency at initial salt solution pH 6 is attributed to the reduction of soluble Cr(VI) to Cr(III) at low concentrations under acidic conditions. The highest efficiency obtained for salt solution metal ion concentration of 20 ppm may be due to the overloading of PEG phase with metal ions for other tested concentrations above 20 ppm.

The optimization studies have been performed using Minitab statistical software version 16. The central composite rotatable design (CCRD) is used to design the experiments by considering two independent variables: (i) initial salt solution pH (ii) metal ion concentration. Operating ranges of the optimization experiments have been selected based on the results obtained in preliminary experiments and further experiments done in triplicate to reduce variability in data collection. The average efficiency and distribution coefficient have been calculated as given below.

$$\text{Percentage extraction efficiency, \% E} = \frac{\text{mass of total Cr extracted to the top phase}}{\text{mass of total Cr in both phases}} \times 100 \quad (1)$$

$$\text{Distribution coefficient, K} = \frac{\text{concentration of total chromium in the top phase}}{\text{concentration of total chromium in the bottom phase}} \quad (2)$$

CCRD with two factors at 5 levels are applied. Table 1 provides the operating parameters and their ranges used in the experiments. Thirteen experiments have been conducted including five replicates at the center point.

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

Independent variables	Coded level				
	$-\alpha$	$-1$	$0$	$+1$	$+\alpha$
Initial salt solution pH	4.58	5	6	7	7.41
Initial metal ion concentration in the aqueous phase (ppm)	5.86	10	20	30	34.14

The efficiency has been found out and analyzed using RSM. A second-order polynomial of the following form is fitted to the experimental data

$$Y = C_0 + C_1X_1 + C_2X_2 + C_{11}X_1^2 + C_{22}X_2^2 + C_{12}X_1X_2 \quad (3)$$

where  $Y$  is the dependent parameter in uncoded units;  $C_0$  is a constant;  $C_1$  and  $C_2$  are regression coefficients representing the linear effects;  $C_{11}$  and  $C_{22}$  are quadratic coefficients;  $C_{12}$  is the interaction coefficient. The extraction efficiency (%) and distribution coefficient for different combinations of two independent variables within the experimental domain of study can be predicted using the model. Analysis of variance (ANOVA) is studied using RSM. The optimal set of parameters that maximize the extraction is determined.

#### 4. Results and discussions

The effectiveness of PEG 1500 - ammonium sulfate aqueous two-phase system for the extraction of hexavalent chromium is studied experimentally and optimized using RSM studies. Experimental results on the metal ion extraction efficiency (%) and distribution coefficient in the various ranges of the independent parameters obtained from the 13 runs as demanded by the CCRD of RSM are tabulated in table 2.

**Table 2.** Experimental data and results of CCRD

Run	pH	Initial metal concentration in the aqueous phase (ppm)	% Efficiency of extraction	Distribution coefficient
1	7	10	22.65	0.83
2	5	10	13.68	0.43
3	6	5.85	19.64	0.63
4	6	20	28.66	0.94
5	5	30	15.91	0.51
6	4.58	20	9.36	0.28
7	6	20	28.42	1.13
8	6	20	27.63	1.09
9	6	20	25.99	1.05

10	7	30	29.80	1.15
11	6	34.14	23.25	0.86
12	6	20	30.34	1.12
13	7.41	20	21.79	0.79

Regression analysis of the data from table 3 is presented by the following quadratic equation (4)

$$Y_1 = -211.94 + 72.41X_1 + 0.595X_2 - 5.818X_1^2 - 0.029X_2^2 + 0.123X_1X_2 \quad (4)$$

Where  $Y_1$  is the extraction efficiency (%) and  $X_1, X_2$  represents initial salt solution pH and initial metal ion concentration in the salt solution in uncoded units.

ANOVA of the % extraction efficiency in coded units is given in table 3. The P-test is used to analyze the significance of the regression coefficients. From the values of P, given in table 3, it can be concluded that both the independent parameters significantly affect the % efficiency of extraction. The F value of 29.62 for regression which is higher than the value of 3.97 in the standard statistical table shows that the model fits well for the design space. The model exhibits a high determination coefficient ( $R^2 = 0.9549$ ) and the adjusted determination coefficient ( $R^2(\text{adj}) = 0.9226$ ), suggesting the high significance of the model. This implies that 95.5% of the variations for the extraction efficiency of Cr ions are explained by the selected independent variables and only 4.5 % of the total variations in the response are not explained by the model.

**Table 3.** ANOVA results for extraction efficiency

Source	DF	Sum of Squares	Mean Squares	F	P	Significance level, (1-P)%
Regression	5	504.049	100.81	29.62	<0.001	> 99
Linear	2	230.598	115.299	33.88	<0.001	> 99
pH	1	204.363	204.363	60.04	<0.001	> 99
Metal ppm	1	26.235	26.235	7.71	0.027	>97
Square	2	267.385	133.693	39.28	<0.001	> 99
pH* pH	1	209.611	209.611	62.82	<0.001	> 99
Metal ppm* Metal ppm	1	57.774	57.774	16.97	0.004	> 99
Interaction	1	6.066	6.066	1.78	0.224	> 77
pH*metal ppm	1	6.066	6.066	1.78	0.224	> 77
Residual Error	7	23.825	3.404			
Lack of fit	3	13.766	4.589	1.82	0.283	Insignificant
Pure error	4	10.059	2.515			

Table 4 gives the regression analysis of the data in coded units and the fitted model obtained for the distribution coefficient is given by the following quadratic equation(5)

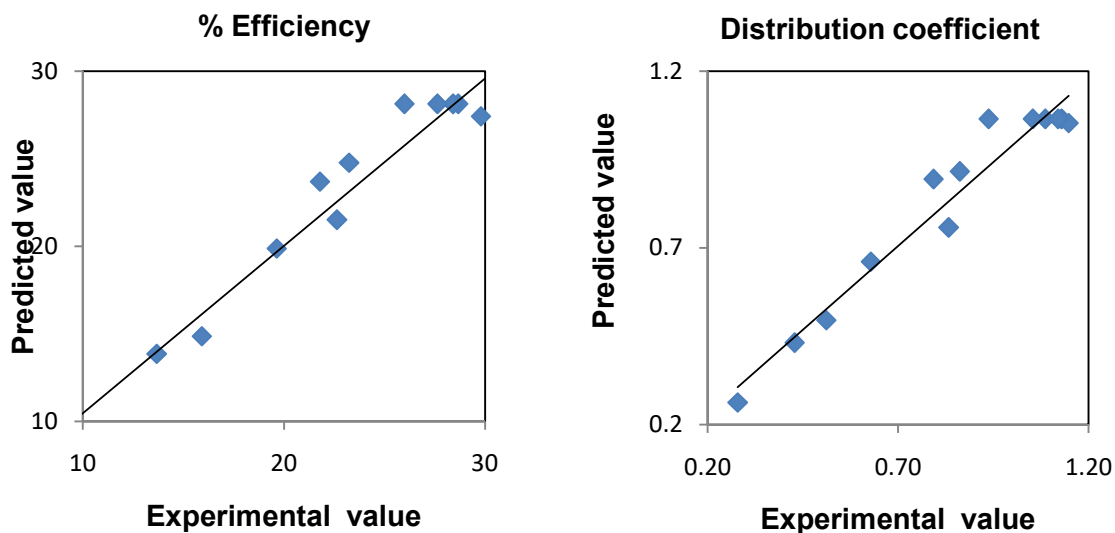
$$Y_2 = -9.0245 + 3.014X_1 + 0.0295X_2 - 0.2424X_1^2 - 0.0014X_2^2 + 0.0058X_1X_2 \quad (5)$$

Here  $Y_2$  is the distribution coefficient and  $X_1, X_2$  represents initial salt solution pH and initial metal ion concentration in the salt solution in uncoded units. The values of P obtained and given in table 4 indicated the significant influence of the independent parameters on the distribution coefficient of metal ions. The F value of 25.29 for regression which is higher than the value of 3.97 in the standard statistical table shows that the model fits well for the design space. The model exhibits a high determination coefficient ( $R^2 = 0.9475$ ) and the adjusted determination coefficient ( $R^2(\text{adj}) = 0.9101$ ), suggesting the high significance of the model.

**Table 4.** ANOVA results for distribution coefficient

Source	DF	Sum of Squares	Mean Squares	F	P	Significance level, (1-P)%
Regression	5	0.9585	0.1917	25.29	<0.001	> 99
Linear	2	0.4567	0.2284	30.12	<0.001	> 99
pH	1	0.3905	0.3905	51.5	<0.001	> 99
Metal ppm	1	0.0663	0.0663	8.74	0.021	>97
Square	2	0.4884	0.2442	32.21	<0.001	> 99
pH* pH	1	0.3565	0.4087	53.91	<0.001	> 99
Metal ppm* Metal ppm	1	0.132	0.1319	17.4	0.004	> 99
Interaction	1	0.0134	0.0134	1.77	0.225	> 77
pH*metal ppm	1	0.0134	0.0134	1.77	0.225	> 77
Residual Error	7	0.0531	0.0076			
Lack of fit	3	0.029	0.0096	1.6	0.323	Insignificant
Pure error	4	0.0241	0.006			

The relationship between the experimental value and the predicted value using the quadratic models are plotted (Figure 1).



**Figure 1.** Comparison of experimental and predicted values of efficiency and distribution coefficient

The responses are optimized using the predicted models and plotted in Figure 2. The optimum efficiency of 29.8 % is predicted. The optimum conditions predicted are salt solution pH of 6.5 and initial salt solution metal concentration 24.43 mg/L. The distribution coefficient of 1.14 is predicted at the optimum conditions. Experiments have been conducted at optimized conditions and average extraction efficiency of 29.33 and a distribution coefficient of 1.16 are obtained. Contour plots of the studied responses are plotted in Figure 3.

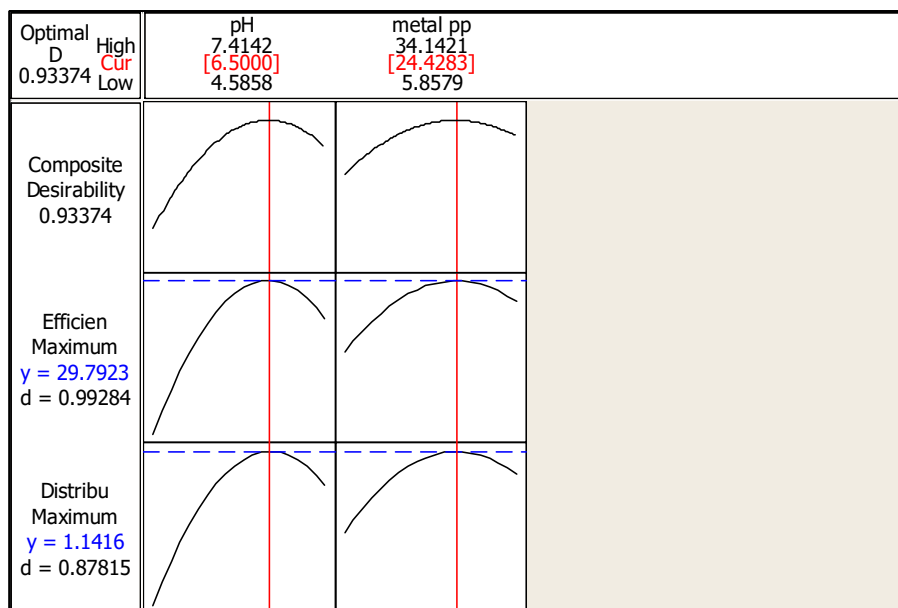


Figure 2 .Optimization plot

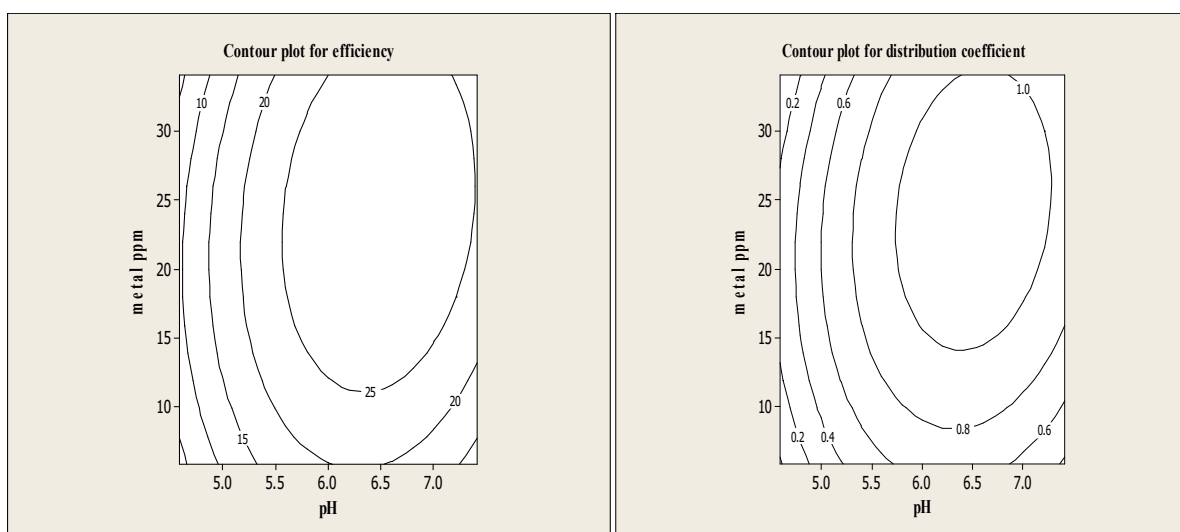


Figure 3. Contour plots of responses

### 5. Conclusions

Aqueous two-phase extraction of metals to PEG from contaminated solutions is considered as a primary method for the recovery of valuable and toxic metals. The extracted metals can be effectively regenerated which in a way helps heading for sustainable development. Studies on the optimization of the heavy metal extraction with aqueous two-phase systems using RSM and the validation using experimental analysis are sparse in the literature. Extraction of hexavalent chromium from contaminated aqueous solutions using PEG 1500 – (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> is optimized using CCD in Minitab statistical software version 16. The maximum efficiency of 29.79% and the distribution coefficient of 1.14 have been achieved for a salt pH of 6.5 and an initial salt phase metal concentration of 24.43 ppm which is in agreement with the experimentally obtained responses. The PEG 1500 being a biodegradable polymer and ammonium sulfate which can be precipitated and recycled after the process by adding methanol enhances the suitability of the process in the context of a sustainable approach and hence the study satisfies the condition of green chemistry despite its low efficiency.

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