

TRIVALENT CHROMIUM REMOVAL BY AQUEOUS TWO-PHASE EXTRACTION WITH CHLORIDE IONS AS EXTRACTANT

S.K. SUJI^{1*} AND K.B. RADHAKRISHNAN²

¹Lal Bahadur Shastri Centre for Science & Technology, University of Kerala,
Thiruvananthapuram 695 033, Kerala, India

¹ Department of Chemical Engineering, Government Engineering College Kozhikode, West Hill,
Kozhikode 673 005, Kerala, India

²Department of Biotechnology and Biochemical Engineering, SCT College of Engineering, Pappanamcode,
Thiruvananthapuram 695 018, Kerala, India

(Received 3 March, 2021; Accepted 8 May, 2021)

ABSTRACT

Trivalent chromium is an essential micronutrient. It is considered as the stable form of chromium. However, the conversion of trivalent to hexavalent chromium in natural conditions is reported by several investigators. Hexavalent chromium is an anthropogenic carcinogen. This necessitates the recycling of chromium from contaminated solutions. The present study focuses on the extraction of trivalent chromium to polyethylene glycol 1500 using sodium chloride as the extractant. The effect of the significant independent parameters as to the initial salt solution pH, extractant concentration and initial salt phase metal ion concentration on the extraction efficiency is studied experimentally. The optimum conditions are found out using central composite design in Minitab statistical software version 16. A second order polynomial model is proposed for the extraction efficiency as a function of the three independent parameters. The maximum efficiency obtained in the present optimization studies is 24.5% at an initial salt solution pH of 4.82, NaCl concentration 0.0035 mol/l and initial metal ion concentration 7.4 ppm. The results of the optimization studies are validated by conducting experiments at the optimum conditions. Extraction of Cr(III) using organic chelating agents may provide better efficiency, but, is not advisable due to recalcitrant and hazardous nature of chemicals involved. The system used in this study satisfies the conditions of green chemistry despite its low efficiency.

KEY WORDS : Aqueous two-phase extraction, Cr(III) extraction, Optimization, PEG 1500 – (NH₄)₂SO₄ system.

INTRODUCTION

Earth's crust is rich with ample resources of chromium and is widely used in industries for tanning, dyeing, electroplating, wood preservation etc. Chromium is a major pollutant in the industrial area causing both surface water and groundwater contamination along with soil contamination. It exists in two stable oxidation states - chromium (III) and chromium (VI). Hexavalent chromium is a powerful oxidising agent and an anthropogenic carcinogen. Chromium (III) is present in nature

predominantly as stable complexes of organic and inorganic ligands (Hartford, 1979). The scientific community was more concerned about the pollution and potential health hazards caused by hexavalent chromium. Conversion of hexavalent chromium to trivalent chromium and disposing it to soil or water was considered as a safe method until Bartlett and James reported (1979, 1983) the oxidation of trivalent chromium to hexavalent chromium under soil environment. The maximum concentration of wastewater discharge permitted by Central Pollution Control Board of India (CPCB India) for

total chromium is 2 ppm. The above findings necessitate the recovery and regeneration of chromium from contaminated solutions irrespective of its oxidation state. Regeneration of Cr(III) is hence more important from economic and environmental perspectives.

Aqueous two-phase extraction (ATPE) of metals is considered as an environmentally benign method. Several scientific papers are available in the regeneration of metals using this technique (Karmakar and Sen, 2018). The ATPE of metal ions such as Zn(II), Ni(II), Cd(II) and Cu(II) are extensively studied by several investigators, however extraction of Cr(III) has not gained much attention.

Aqueous two-phase systems are composed of two polymer systems, polymer-salt systems, polymer-ionic liquid systems, two salt systems, or ionic liquids-salt systems. Among these, polymer-salt systems are more economically viable. Polyethylene glycols (PEGs) with average molecular weight (1200-6000) are commonly used in ATPE of metal ions due to their biocompatibility, low cost, and low volatility (Karmakar and Sen, 2018). In this study, PEG 1500-ammonium sulphate two phase system is used. Rapid phase separation and clear interface can be obtained with 40% (w/w) PEG 1500 and 40% (w/w) ammonium sulphate system (Gao *et al.*, 1991).

Organic chelating agents, thiocyanates, or halides are used as extracting agents to enhance the extraction of cationic metal ions to organic phase, which in turn increases the hydrophobicity of metal ions. Cr(III) is a hard acid which can be extracted with chloride ions or chelating agents (Atkins *et al.*, 2009). The commonly used chelating agents for metal extraction in ATPE are dithizone, 1-(2-pyridylazo)-2-naphthol, 1-Nitroso-2-naphthol, 8-hydroxyquinoline etc. All these are recalcitrant chemicals and are harmful to biotic life. Considering the environmental friendliness, bulk availability and economy sodium chloride is selected as extracting agent in this work.

This paper presents the studies carried out to determine the efficiency of Cr(III) extraction in PEG 1500 - ammonium sulfate system at a constant temperature. The effect of significant parameters on the extraction of trivalent chromium is analysed by response surface methodology and further optimized using central composite design (CCD) in MINITAB statistical software version 16. The significant parameters analysed are the stock salt

solution pH, initial metal ion concentration, and NaCl concentration in the PEG 1500 - ammonium sulphate system under constant temperature.

MATERIALS AND METHODS

Materials and instruments

Polyethylene glycol (Molecular Weight 1500) has been obtained from Loba Chemie Pvt. Ltd. (Mumbai, India), chromium nitrate nonahydrate from Sigma Aldrich, ammonium sulphate from Merck life science Pvt. Ltd. (Mumbai, India) and sodium chloride from Isochem laboratories (Kochi, India). The above chemicals were used for experiments without further purification. Double distilled water is used throughout the experiment.

Atomic Absorption Spectrophotometer (Thermo Scientific iCE3000 series) is used for the determination of total chromium concentration. Salt stock solution pH is adjusted using 0.1 N, H_2SO_4 and NaOH and measured using pH meter (Eutech instruments pH Tutor).

Procedure

Chromium nitrate nonahydrate was dissolved in double distilled water to prepare 1000 ppm Cr(III) stock solution. The solution was diluted to different concentrations as per requirement. Suitable quantity of solid PEG with an average molecular weight of 1500 g/mol was dissolved in double distilled water. The salt solution was prepared by dissolving required quantity of $(NH_4)_2SO_4$ in double distilled water. 1 mol/l sodium chloride solution was prepared and further diluted as per requirement.

Extraction Procedure

The batch type extraction experiments were carried out at a constant temperature of 30 °C. Four ml of the pH adjusted 40% (w/w) $(NH_4)_2SO_4$ salt solution was mixed with 1 ml of known concentration of NaCl and 1 ml of desired concentration of chromium nitrate solution. 4 ml of 40% (w/w) PEG solution was consequently added to the above solution. The contents were shaken in an orbital shaker for 10 minutes and kept overnight in a water bath. The solution was centrifuged at 1500 rpm for 10 minutes. Organic phase and salt phase was carefully separated using a Pasteur pipette. 1ml of the top (organic) phase solution was diluted and analyzed in atomic absorption spectrophotometer for the chromium concentration. Experiments were

done in triplicate to reduce variability in data collection and the average efficiency is reported. The extraction efficiency (E) is given by the equation

$$\% E = \frac{\text{Mass of total chromium extracted to the top phase}}{\text{Mass of trivalent chromium added}} \dots (1)$$

Design of experiments and modelling using Response Surface Methodology (RSM)

The preliminary experiments were conducted for various ranges of (i) salt stock solution pH, (ii) extractant concentration and (iii) initial concentration of trivalent chromium in the salt phase. The ranges of variables selected include the initial salt solution pH of 3-7, metal ion concentration of 10 -100 ppm in the salt phase and NaCl concentration of 0.001-0.06 mol/l. Based on the results obtained from preliminary experiments, design of experiments were performed using Minitab statistical software version 16 (PA,USA). The central composite design (CCD) was used for experiment design. The CCD with three factors at 5 levels was applied. Independent variables and levels selected for the design of experiments are given in Table 1. Twenty experiments were performed with five replicates at the center point.

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

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

Where Y is the response in coded units; C_0 is the regression constant; C_1, C_2, C_3 are regression coefficients for linear effects; C_{11}, C_{22}, C_{33} are quadratic coefficients; $C_{12}, C_{13},$ and C_{23} are the interaction coefficients. Using the model the extraction efficiency (%) for different combination of three independent variables within the experimental domain of parameters can be predicted. Analysis of variance (ANOVA) was performed using RSM and the optimal set of parameters that maximize the efficiency was determined.

RESULTS AND DISCUSSION

The effectiveness of extraction of trivalent chromium using PEG 1500 - $(\text{NH}_4)_2\text{SO}_4$ aqueous two-phase system with sodium chloride as extractant was studied experimentally. The significant parameters were optimized using RSM studies and a second order polynomial model was developed to predict the extraction efficiency in terms of the significant independent parameters.

Preliminary experiments

Influence of concentration of extracting agent on extraction efficiency

The effect of the extracting agent concentration on the extraction of trivalent chromium was investigated. The NaCl concentration used in the experiments was varied from 0.001 mol/l to 0.06 mol/l at a constant pH of 5 and metal concentration of 20 ppm. The maximum efficiency obtained in the preliminary experiments conducted in the study is 20.3 % at a concentration of 0.01 mol/l of the extractant. Further decrease in the extraction efficiency has been observed in the experiments for extractant concentrations above 0.01 mol/l. This decrease in efficiency at higher chloride ion concentration may be due to the formation of unstable hydrophilic chromium chloride anionic complexes.

Influence of ammonium sulfate solution pH on extraction efficiency

The salt stock solution pH is an important parameter that determines the distribution of metal ions between the two phases. The pH of the salt stock solution is varied from 3 to 7 at an extractant concentration of 0.01 mol/l and initial metal ion concentration in the salt phase at 20 ppm. The maximum efficiency is obtained at a pH of 5. Blázquez *et al.*, (2009) reported that chromium nitrate in water exists as trivalent chromium at $\text{pH} < 3$; the level of Cr^{3+} and $\text{Cr}(\text{OH})^{2+}$ is in equal proportions at $3 < \text{pH} < 4$ and $\text{Cr}(\text{OH})^{2+}$ is

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

| Independent variables | Coded level ($\alpha = 1.2$) | | | | |
|--|--------------------------------|-------|--------|------|-----------|
| | $-\alpha$ | -1 | 0 | +1 | $+\alpha$ |
| Salt stock solution pH | 3.8 | 4 | 5 | 6 | 6.2 |
| Initial metal ion concentration in the aqueous phase (ppm) | 0.2 | 2 | 11 | 20 | 21.8 |
| Extracting agent, NaCl concentration (mol/L) | 0.0035 | 0.005 | 0.0125 | 0.02 | 0.0215 |

predominant at $4 < \text{pH} < 6.5$. $\text{Cr}(\text{OH})_3$ is the major species available at pH between 6.5 and 11 and above which $\text{Cr}(\text{OH})_4^-$ is more prevalent. The higher extraction efficiency yielded at a pH of 5 can be attributed to the existence of $\text{Cr}(\text{OH})^{2+}$.

Influence of trivalent chromium ion concentration on extraction efficiency

Trivalent chromium concentration in the salt phase has been varied from 10 ppm - 100 ppm with extracting agent concentration 0.01 mol/l and salt solution pH 5. Maximum extraction efficiency is observed at a metal concentration of 10 ppm and thereafter a reduction in extraction efficiency is observed with further increase in the metal concentration above 10 ppm. The decrease in efficiency is attributed to the overloading of PEG phase with the metal ions. Similar observations were reported for the extraction of Zn (II) ions using PEG - 1550/ $(\text{NH}_4)_2\text{SO}_4$ aqueous two phase extraction systems and for the extraction of Cu(II) ions using the PEG 2000 - sodium sulfate system (Khayati *et al.*, 2016).

Modeling using response surface methodology

The Cr(III) ion extraction efficiency (%) was found out for 20 experimental conditions based on CCD of RSM and is given in Table 2 given below.

The second order polynomial model obtained by

regression analysis of the data of table 2 is given in equation 3.

$$y = -89.7917 + 47.938 X_1 + 0.6786 X_2 - 1530.54X_3 - 4.962X_1^2 - 0.0355X_2^2 + 15139.2X_3^2 - 0.557X_1X_2 + 99.85X_1X_3 + 34.34X_2X_3 \quad \dots (2)$$

where Y is the extraction efficiency (%) and X_1, X_2, X_3 are respectively the salt solution pH, initial salt phase metal ion concentration (mg/l) and NaCl concentration (mol/l) in uncoded units. ANOVA of the % extraction efficiency is given in Table 3 given below.

The significance of regression coefficients was analysed by the Fisher's F-test. From the values of probability of occurrence (P), given in Table 3 it can be seen that all three terms representing the independent variables significantly affect the efficiency of extraction of the system. A higher F-value of 41.54 for regression than the given value of 3.02 in the standard statistical table shows the adequacy models. The high determination coefficient ($R^2 = 0.974$) and the adjusted determination coefficient ($R^2_{\text{adj}} = 0.95$), implies the high significance of the model. A small deviation between the determination coefficient and the adjusted determination coefficient eliminates the chance of including other parameters into the model and implies that the model is highly significant. The response optimisation is carried out using RSM and

Table 2. Experimental data

| Run Order | Initial salt phase pH | Initial Cr(III) concentration (mg/l) | NaCl concentration (mol/l) | Efficiency |
|-----------|-----------------------|--------------------------------------|----------------------------|------------|
| 1 | 5 | 11 | 0.0125 | 20.635 |
| 2 | 5 | 11 | 0.0125 | 19.350 |
| 3 | 5 | 11 | 0.0215 | 19.67 |
| 4 | 4 | 2 | 0.02 | 7.764 |
| 5 | 4 | 2 | 0.005 | 18.600 |
| 6 | 5 | 11 | 0.0035 | 23.184 |
| 7 | 6 | 20 | 0.005 | 11.380 |
| 8 | 5 | 11 | 0.0125 | 19.340 |
| 9 | 6 | 2 | 0.005 | 15.670 |
| 10 | 5 | 0.2 | 0.0125 | 16.076 |
| 11 | 4 | 20 | 0.005 | 16.026 |
| 12 | 6.2 | 11 | 0.0125 | 12.113 |
| 13 | 5 | 11 | 0.0125 | 21.800 |
| 14 | 5 | 11 | 0.0125 | 18.705 |
| 15 | 4 | 20 | 0.02 | 14.750 |
| 16 | 5 | 11 | 0.0125 | 20.860 |
| 17 | 6 | 2 | 0.02 | 8.119 |
| 18 | 3.8 | 11 | 0.0125 | 13.997 |
| 19 | 5 | 21.8 | 0.0125 | 16.050 |
| 20 | 6 | 20 | 0.02 | 12.810 |

Table 3. ANOVA results for extraction efficiency

| Source | DF | Sum of Squares | Mean Squares | F | P | Significance level (1-P)% |
|---------------------------|----|----------------|--------------|--------|-------|---------------------------|
| Model | 9 | 350.78 | 38.98 | 41.54 | 0.001 | > 99 |
| Linear | 3 | 60.415 | 20.14 | 21.46 | 0.001 | > 99 |
| X_1 (pH) | 1 | 11.99 | 11.99 | 12.78 | 0.005 | > 99 |
| X_2 (Cr ³⁺) | 1 | 2.1 | 2.102 | 2.24 | 0.165 | 83.5 |
| X_3 (NaCl) | 1 | 46.323 | 46.323 | 49.37 | 0.001 | > 99 |
| Square | 3 | 240.893 | 80.298 | 85.57 | 0.001 | > 99 |
| | 1 | 197.979 | 127.701 | 136.09 | 0.001 | > 99 |
| | 1 | 39.153 | 42.818 | 45.63 | 0.001 | > 99 |
| | 1 | 3.761 | 3.761 | 4.01 | 0.073 | 92.7 |
| Interaction | 3 | 49.469 | 16.49 | 17.57 | 0.001 | > 99 |
| X_1, X_2 | 1 | 2.011 | 2.011 | 2.14 | 0.174 | 82.6 |
| X_1, X_3 | 1 | 4.487 | 4.487 | 4.78 | 0.054 | 94.6 |
| X_2, X_3 | 1 | 42.971 | 42.971 | 45.79 | 0.001 | > 99 |
| Residual error | 10 | 9.383 | 0.938 | | | |
| Lack of fit | 5 | 2.545 | 0.509 | 0.37 | 0.849 | Insignificant |
| Pure error | 5 | 6.839 | 1.368 | | | |

results are plotted in Figure 1 given below.

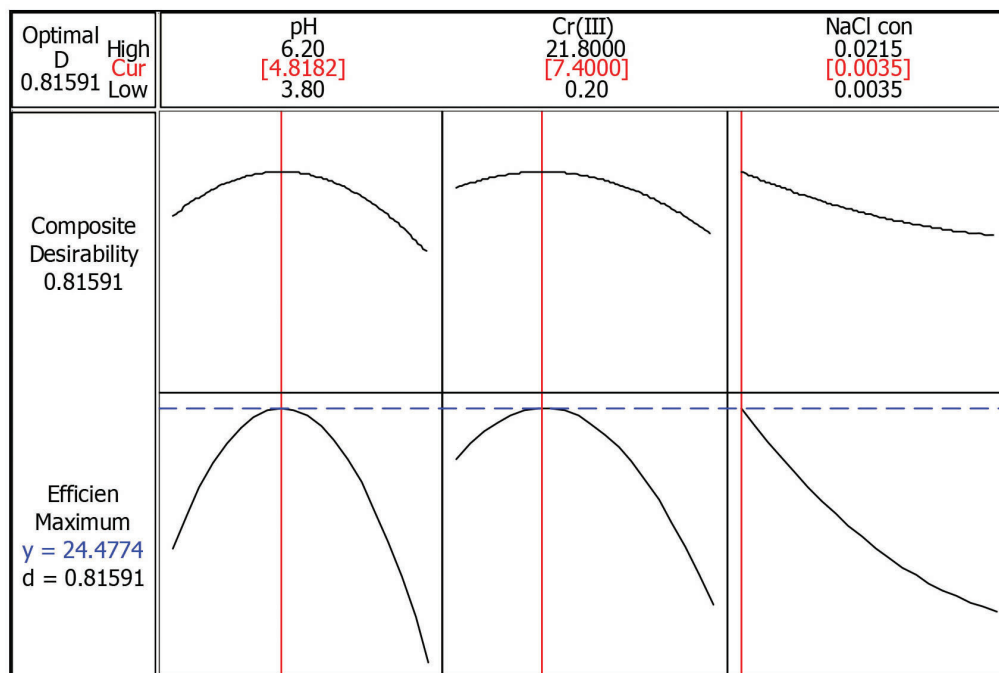
The maximum extraction efficiency was obtained at a pH 4.8, metal concentration 7.4 ppm and NaCl concentration 0.0035 mol/l. Experiments were conducted at the conditions corresponding to these optimum set of parameters and average extraction efficiency of 24.5% was observed.

The circular nature of contour plot of extraction efficiency versus Cr(III) concentration and salt stock solution pH implies that there exists a peak for both

parameters. From the contour plots it is clear that lower concentrations of chloride ions favours extraction in the studied range.

CONCLUSION

Trivalent chromium is extracted using PEG 1500 – (NH₄)₂SO₄ aqueous two phase system with sodium chloride as extracting agent. Significant parameters selected for the study are initial salt solution pH,

**Fig. 1.** Optimization plot

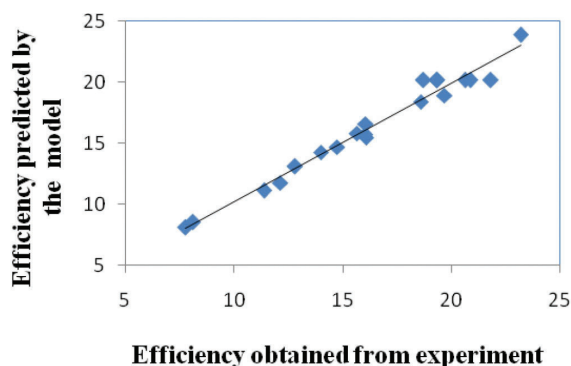


Fig. 2. Comparison of experimental and predicted values of efficiency

initial salt phase metal ion concentration and NaCl concentration. Preliminary experiments are conducted and range for variables for optimisation study is decided. Experiment design, modelling and optimization are carried out using CCD in Minitab statistical software version 16. The model yielded a maximum efficiency of 24.5% at an initial salt solution pH of 4.8, chloride ion concentration 0.0035 mol/l and an initial salt phase metal ion concentration of 7.4 ppm. The model is validated by

conducting experiments under optimum conditions obtained from the model.

Chromium is an industrially important metal, but it causes severe pollution and affects both flora and fauna. Chromium recycling has to be done irrespective of its oxidation state. Unlike other solvents used in chromium extraction processes reported in literature, the present study assumes significance due to the fact that the PEG 1500 used for extraction is a non toxic and biodegradable. Further, ammonium sulphate used in the process can also be regenerated by precipitation by addition of methanol. Thereby sustainability of the process can be enhanced. The study is also significant as the PEG1500- $(\text{NH}_4)_2\text{SO}_4$ system with NaCl as extracting agent can be used for the primary separation of trivalent chromium from contaminated solutions in the most eco-friendly manner.

REFERENCES

Atkins, Peter, Tina Overton, Jonathan Rourke, Mark Weller, and Fraser Armstrong. 2009. Shriver and Atkins' Inorganic Chemistry. Great Britain by Oxford University Press.

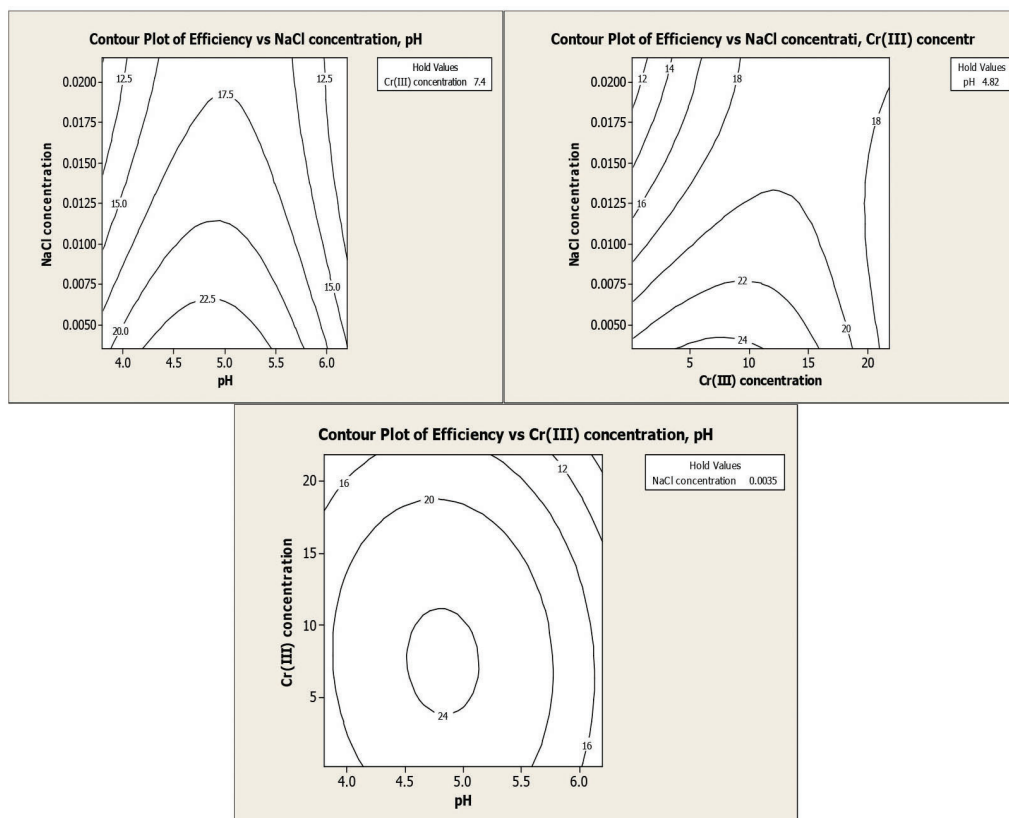


Fig. 3. Contour plots of various parameters

- Bartlett, R.J. and James, B. 1979. Behavior of chromium in soils. Part III: oxidation. *J. Environ. Qual.* 8: 31-35.
- Bartlett, R.J. and James, B.R. 1983. Behavior of chromium in soils. Part VI: interactions between oxidation-reduction and organic complexation. *J. Environ. Qual.* 12 : 173-176.
- Blázquez, G., Hernáinz, F., Calero, M., Martín-Lara, M. A. and Tenorio, G. 2009. The Effect of pH on the Biosorption of Cr (III) and Cr (VI) with Olive Stone. *Chemical Engineering Journal.* 148 (2-3): 473-79.
- Environment Standards for Ambient Air, Automobiles, Fuel, Industries and Noise. 2000. *Central Pollution Control Board*, Ministry of Environment and Forests. 55-56.
- Gao, Yun Long, Qin Hua Peng, Zong Cheng Li, and Yi Gui Li. 1991. Thermodynamics of Ammonium Sulfate-Polyethylene Glycol Aqueous Two-Phase Systems. Part1. Experiment and Correlation Using Extended Uniquac Equation. *Fluid Phase Equilibria.*
- Hartford, W.H. 1979. Chromium compounds. p 82-120. In: Grayson M and Eckroth D (eds) *Kirk-Othmer Encyclopedia of Chemical Technology*. Vol 6. John Wiley and Sons, New York.
- Karmakar, R. and Kamalika Sen. 2018. Aqueous biphasic extraction of metal ions: An alternative technology for metal regeneration. *Molliq.*
- Khayati, G., Gilani, H. G. and Keyvani, Z. S. 2016. Extraction of Cu(II) ions from aqueous media using PEG/Sulphate salt aqueous two-phase system. *Sep. Sci. Technol.* (Philadelphia) 51 (4) : 601-608.
- Laura Bulgariu and Dumitru Bulgariu. 2007. The Extraction of Zn(II) in Aqueous PEG (1550) - (NH₄)₂SO₄ Two-Phase System Using Cl⁻ Ions as Extracting Agent. *Journal of the Serbian Chemical Society.* 72 (3): 289-97.
- Montgomery, Douglas C. 2012. Design and Analysis of Experiments Eighth Edition. Design. <https://doi.org/10.1198/tech.2006.s372>.
- Montgomery, Douglas, C., George C. Runger, and Norma F. Hubele. 2013. *Engineering Statistics*. Fifth. Wiley.