

Removal of Copper Ions from Acid Mine Drainage Wastewater Using Ion Exchange Technique: Factorial Design Analysis

R. W. Gaikwad¹, R. S. Sapkal², V. S. Sapkal²

¹Department of Chemical Engineering, Pravara Rural Engineering College, Loni, Dist: Ahmednagar (MS), India

²Department of Chemical Technology, Sant Gadgebaba Amravati University, Amravati (MS), India

E-mail: rwgaikwad@yahoo.com

Received July 8, 2010; revised July 13, 2010; accepted July 19, 2010

Abstract

A factorial experimental design method was used to examine the “Cu²⁺” removal from acid mine drainage wastewater by ion exchange technique. Ion Exchange technique is preferred because of reduced sludge generation compared to conventional treatment techniques and better decontamination efficiency from highly diluted solutions. Factorial design of experiments is employed to study the effect of four factors pH (3, 5, and 6), flow rate (5, 10, 15 L/hr), resin bed height (20, 40 and 60 cm) and initial concentration of the metal (100, 150 and 200 mg l⁻¹) at three levels. The efficiency of metal removal was determined after 100 min of treatment. Main effects and interaction effects of the four factors were analyzed using statistical techniques. A regression model was recommended and it was found to fit the experimental data very well. The results were analyzed statistically using the Student’s t-test, analysis of variance, F-test and lack of fit to define most important process variables affecting the percentage “Cu²⁺” removal. In this study, pH was thus found to be the most important variable.

Keywords: Acid Mine Drainage, Ion Exchange, Heavy Metal, Copper, Removal, Factorial Design of Experiments

1. Introduction

Acid mine drainage (AMD) continues to be an important water pollution problem in mining industry around the world. When sulphide/pyretic minerals are exposed to the atmosphere, in presence of water oxidation of sulphide produces sulphuric acid and releases heavy metals and other pollutants to the drainage. When sulphide minerals are processed in mineral processing units releases acidic effluents and also contains some other toxic substances, which are used in mineral processing. Further, the mill tailings amount to about 90% of ore is dumped in tailing impoundments and seepage from these impoundments can be source of acid mine drainage. AMD is often characterized by low pH water with elevated concentrations of iron, sulphates and heavy metals of varying composition dependent upon the originating mineral deposit types. The metal load is of greater concern than the acidity in the terms of environmental damage [1-5]. An hazardous feature of AMD is that its

sources may remain active for decades or even centuries after mine closure [6]. Both operating and abandoned polymetallic sulphide mining sites are often active sources of AMD.

Several techniques such as chemical precipitation, oxidation, reduction, coagulation, solvent extraction, and adsorption have been commonly employed for the removal of metal ions. A review of treatments have been presented by Gaikwad and Gupta (7). Among these, ion exchange has been found to be efficient and economically feasible as a wastewater treatment operation. Several adsorbents can be used to remove metal ions, including activated carbons, alumina, silica, bentonite and peat. Yi et.al. [8-10] has also studied the removal of inorganic metal ions namely cadmium, cobalt, zinc, silver, copper, mercury, chromium and lead from aqueous solution by using different adsorbents. Ion exchange resins with improved sorption capacity as well as adsorbents may have advantages over such non-specific adsorbents [11]. In this regard, ion exchange resins hold great po-

tential for the removal of heavy metals from water and industrial wastewater [12,13].

In the present study, Indion 730 cation exchange resins were used for the removal of copper from aqueous solution. In a multivariate experiment, all of the important variables are changed during each run of trials. The need for this arises because the variables often interact with each other. For example, if pH conditions are optimized at one concentration, this work may have to be repeated if it is subsequently found that a different concentration works better.

In a multivariate approach, variation of concentration is included in the first round of experiments. This will show the best direction to move within the multidimensional space defined by the major variables. There are several important problems with the conventional approach of changing only one or two variables in a run. Several experimental runs have to be conducted in order to find the optimum point. In cases where variables must be changed in large steps, the optimum may not be found at all. The factorial design would reveal the effect of the interaction of process variables and improve optimization process. The relative importance of all the factors can be evaluated simultaneously with less number of experiments [14-16]. Flow rate, pH, initial concentration of metal solution and resin dosage are important parameters in ion exchange. Thus in the present study, capacity of Indion 730 to remove "Cu²⁺" was investigated by varying these factors at three levels. Interaction between these factors were studied and optimization done.

2. Materials and Methods

2.1. Ion Exchange Resin

The anion exchange resins Indion 730 (supplied by Ion Exchange India Limited, India) used in this study are used for the removal of heavy metal. Their physical properties and specifications are presented in **Table 1**.

2.2. Preparation of Cu (II) Solution

A stock solution of "Cu²⁺" (1000 mg l⁻¹) was prepared by

Table 1. Characteristics properties of the ion exchange resins used Indion 730 (Strong Acid Cation Exchange Resin).

Physical form	Greyish coloured spherical beads
Ionic form as supplied	Hydrogen, (H + form)
Moisture holding capacity	54 – 57%
Particle size	0.3 – 1.2 mm
Uniformity coefficient	1.7 max.
Total exchange capacity	1.7 meq / ml
pH range	0 – 14
Shipping weight	800 gm/lit

dissolving 3.929 g of CuSO₄.5H₂O (Sd. Fine Chemicals Mumbai) in distilled water. The stock solution was diluted as required to obtain standard solutions 0 to 250 mg l⁻¹ of "Cu²⁺".

2.3. Column Study

The four factors initial concentration of "Cu²⁺", pH, flow rate and resin dosage are varied at three levels as shown in the **Table 2**. For each run, 25 litres of the "Cu²⁺" solution was passed through the column made of glass at 5 litres per hour for 100 minutes. The height and diameter of the column was 100 cm and 5 cm respectively. Samples were analysed using Chemito 201 make atomic absorption spectrophotometer at a maximum wavelength of 324.8 nm. Eighty one experiments with all possible combinations of variables were conducted and a matrix was established according to their high, middle and low levels, represented by +1, 0 and -1, respectively.

3. Results and Discussion

The percent removal was defined as

$$\% R = \left(\frac{C_o - C_e}{C_o} \right) \times 100 \quad (1)$$

where C_o is initial concentration and C_e is the final concentration of the metal in the solution.

The results were analyzed using MINITAB 14 for windows. The main effects and interaction between factors were determined. The effect of a factor is the change in response, here, percentage of metal removal produced by a change in the level of a factor, pH, flow rate, initial concentration of "Cu²⁺" or bed height, from lower to higher level.

The codified model employed for 3⁴ factorial designs was

$$\begin{aligned} \eta = & A_0 + A_1X_1 + A_2X_2 + A_3X_3 + A_4X_4 + A_5X_1X_2 \\ & + A_6X_1X_3 + A_7X_1X_4 + A_8X_2X_3 + A_9X_2X_4 \\ & + A_{10}X_3X_4 + A_{11}X_1X_2X_3 + A_{12}X_1X_2X_4 \\ & + A_{13}X_1X_3X_4 + A_{14}X_2X_3X_4 \end{aligned} \quad (2)$$

where A₀ represents the global mean and A_i represents the regression coefficient corresponding to the main factor effects and interactions. The effects, regression coef-

Table 2. Levels of factors.

Factor	Low (-1)	Middle (0)	High (+1)
Concentration, mg l ⁻¹	100	150	200
pH	3	5	6
Bed Height, cm.	20	40	60
Flow Rate, LPH	5	10	15

ficients, standard errors, and P are shown in **Table 3**. The main effects represent deviations of the average between high and low levels for each one of them. When the effect of a factor is positive, percentage removal increase as the factor is changed from low to high levels. In contrast, if the effects are negative, a reduction in percent removal occurs for high level of the same factor. **Figure 1** shows the main effects of the four factors on percentage metal removal. Substituting the regression coefficients in equation (2) we get model equation relating the level of parameters and metal removal.

$$\eta = 29.81 + 20.55X_1 - 5.24X_2 - 3.35X_3 - 0.42X_4 + 0.47X_1X_2 - 3.14X_1X_3 + 1.83X_1X_4 - 0.83X_2X_3 + 1.56X_2X_4 - 1.04X_3X_4 + 3.53X_1X_2X_3 - 1.89X_1X_2X_4 + 4.15X_1X_3X_4 - 2.15X_2X_3X_4 \quad (3)$$

3.1. Student’s t-test

The Pareto chart (**Figure 2**) gives the relative importance of the individual and interaction effects. Student’s t-test

Table 3. Statistical Analysis.

Term	Coeff.	SE Coeff.	T	P
Constant	29.8151	0.5632	52.93	0.000
Con	20.5553	0.7965	25.81	0.000
pH	-5.2417	0.7965	-6.58	0.000
Bed	-3.4521	0.7965	-4.33	0.001
Flow	-0.4291	0.7965	-0.54	0.597
Con*pH	0.478	1.126	0.42	0.677
Con*Bed	-3.140	1.126	-2.79	0.013
Con*Flow	1.837	1.126	1.63	0.122
pH*Bed	-0.838	1.126	-0.74	0.468
pH*Flow	1.562	1.126	1.39	0.184
Bed*Flow	-1.046	1.126	-0.93	0.367
Con*pH*Bed	3.534	1.593	2.22	0.041
Con*pH*Flow	-1.899	1.593	-1.19	0.251
Con*Bed*Flow	4.157	1.593	2.61	0.019
pH*Bed*Flow	-2.150	1.593	-1.35	0.196

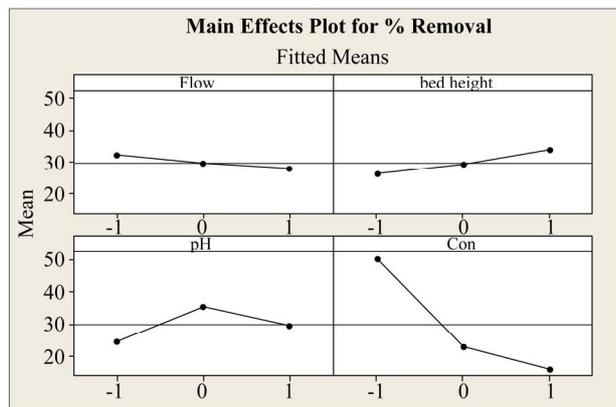


Figure 1. Main effects plot for percentage removal (%R).

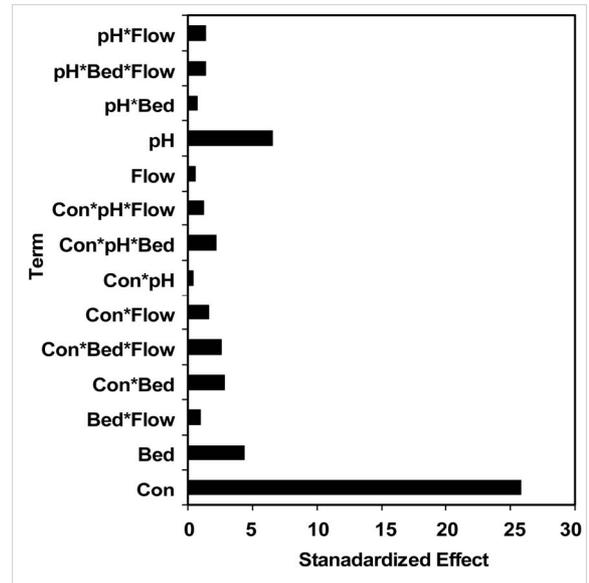


Figure 2. Pareto Chart.

was performed to determine whether the calculated effects were significantly different from zero and these values for each effect are shown in Pareto chart by horizontal columns. For a 95% confidence level and eighty degrees of freedom t-value is equal to 5.

3.2. Analysis of Variance (ANOVA)

In **Table 4** the sum of squares used to estimate the factors’ effects and F-ratios are shown. The effects are statistically significant when P-value, defined as the smallest level of significance leading to rejection of null hypothesis. Based on the student’s t-test and F-test, few interaction effects which seem insignificant compared to other effects, were neglected and the effects, regression coefficients, standard error, t and p-value were recalculated with remaining variables. Resultant values are shown in **Table 5**. Reduced model equation with resultant coefficients was

$$\eta = 29.81 - 20.55A - 5.24B - 3.45C - 0.42D + 0.09AB - 0.93BC + 2.08CD \quad (4)$$

For the reduced model ANOVA and F-test and were performed and results of ANOVA are given in **Table 6**. Interaction plot of effects is shown in **Figure 3**. Lack of fit associated elimination of few factors was $F = 0.88$. Therefore, these factors did not have statistical significance. The residues should also be examined for normal distribution. **Figure 4** shows normal probability plot of residual values. It could be seen that the experimental points were reasonably aligned suggesting normal distribution. Plot of percentage removal versus residual (**Figure 4**) indicated the outliers if any.

Table 4. Full factorial design analysis.

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Con	2	17752.89	17752.89	8876.45	345.44	0.000
pH	2	1607.08	1607.08	803.54	31.27	0.000
Bed	2	758.00	758.00	379.00	14.75	0.000
Flow	2	223.38	223.38	111.69	4.35	0.031
Con*pH	4	762.12	762.12	190.53	7.41	0.001
Con*Bed	4	271.60	271.60	67.90	2.64	0.072
Con*Flow	4	84.84	84.84	21.21	0.83	0.528
pH*Bed	4	98.32	98.32	24.58	0.96	0.458
pH*Flow	4	50.38	50.38	12.59	0.49	0.743
Bed*Flow	4	88.60	88.60	22.15	0.86	0.508
Con*pH*Bed	8	164.12	164.12	20.52	0.80	0.613
Con*pH*Flow	8	130.39	130.39	16.30	0.63	0.738
Con*Bed*Flow	8	182.67	182.67	22.83	0.89	0.547
pH*Bed*Flow	8	216.20	216.20	27.02	1.05	0.441
Error	16	411.14	411.14	25.70		
Total	80	22801.73				

Table 5. Statistical Analysis for Reduced design.

Term	Coeff.	SE Coeff.	T	P
Constant	29.8151	0.5577	53.47	0.000
Con	20.5553	0.7886	26.06	0.000
pH	-5.2417	0.7886	-6.65	0.000
Bed	-3.4521	0.7886	-4.38	0.000
Flow	-0.4291	0.7886	-0.54	0.588
Con*pH	0.094	1.115	0.08	0.933
pH*Bed	-0.838	1.115	-0.75	0.455
Bed*Flow	2.088	1.115	1.87	0.066

Table 6. Analysis of Variance for % Removal Reduced design.

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Con	2	17752.9	17752.9	8876.4	352.39	0.000
pH	2	1607.1	1607.1	803.5	31.90	0.000
Bed	2	758.0	758.0	379.0	15.05	0.000
Flow	2	223.4	223.4	111.7	4.43	0.016
Con*pH	4	762.1	762.1	190.5	7.56	0.000
pH*Bed	4	98.3	98.3	24.6	0.98	0.428
Bed*Flow	4	88.6	88.6	22.2	0.88	0.482
Error	60	1511.3	1511.3	25.2		
Total	80	22801.7				

S = 5.01887 R-Sq = 93.37% R-Sq(adj) = 91.16%

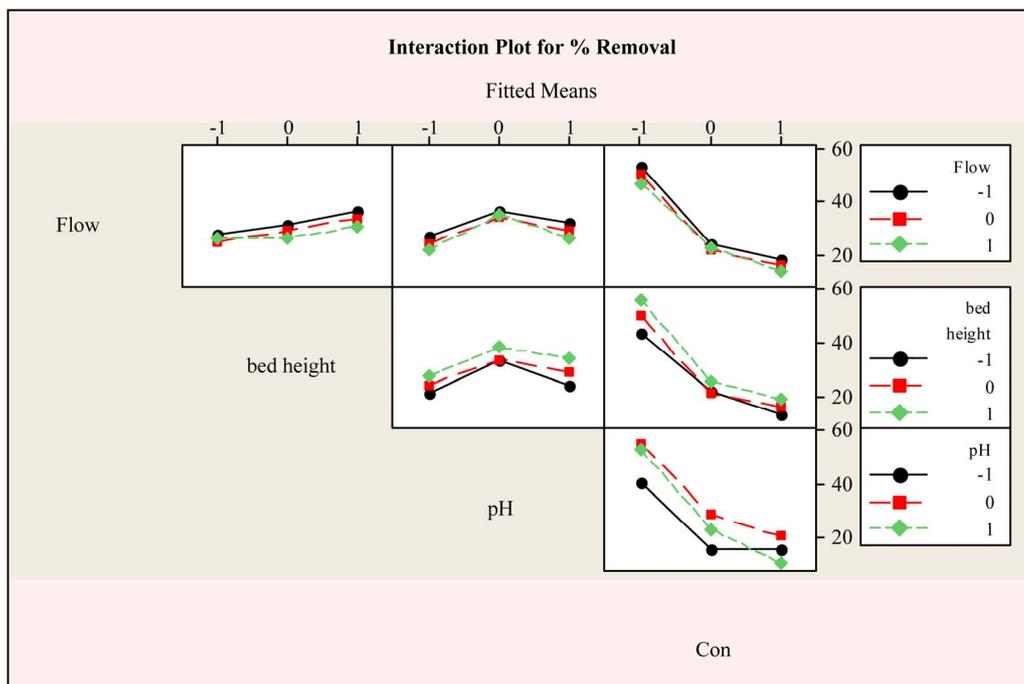


Figure 3. Interaction effects for percentage Cu(II) removal.

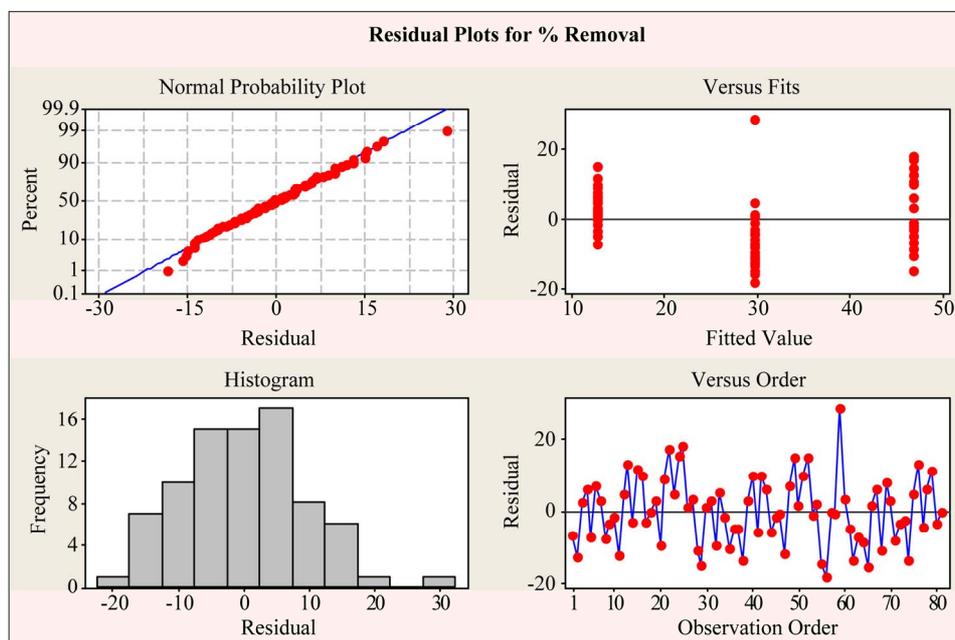


Figure 4. Normal probability plot of residual values for removal efficiency of Cu(II) vs. their expected values when the distribution is normal.

3.3. Effect of pH

pH plays a major role in removal of “Cu²⁺”. As indicated in **Table 3**, shows that pH has a significant effect. Increase in pH from 3 to 5 increases the adsorption efficiency by about 10%. and then increase in pH from 5 to 6 decreases the adsorption efficiency by about 5%. pH equal to 5 favours adsorption of metal on Indion 730.

3.4. Effect of Bed Height, Flow Rate and Initial Concentration of Metal

Adsorption rate increase, as expected, with increase in adsorbent dosage. Increase of resin dosage i.e. bed height from 20 cm to 60 cm, increases adsorption rate by 7%. This is due to the fact that increases in adsorbent dosage increase area available for adsorption. Also as expected increase of initial concentration decrease adsorption rate. Increase from 100 to 200 mg l⁻¹ result in decrease of removal efficiency by 40%. At higher concentration, adsorption efficiency decrease due to saturation of all adsorption sites. Apart from these linear effects of the parameters used, the interaction between these parameters gives better explanation of the process. As mentioned above F-test and student’s t-test were used to study the interaction effects.

Interaction plot (**Figure 3**) clearly indicates strong interaction between initial concentration of metal, pH, bed height and flow rate. The % metal removal is found to be maximum at pH equal to 5. When pH is increased from 3

to 5, removal efficiency increases from 20% to 27% at 20cms bed height and 32 to 36 % at 60cms bed height. That is the effect of pH is high when the dosage is low, but at higher dosage pH effects are not that much high. Similarly at low concentration, metal removal efficiency was only 44 and 54% at 20cms and 60cms bed height, respectively. But at higher initial concentration, 200 mg l⁻¹, change bed height from 20 cms to 60cms increases metal removal efficiency by 12%, i.e. from 8 to 20%. Similarly change in bed height produced 3% and 5% decrease in percentage metal removal at lower and higher flow rates respectively. Also change in pH from 3 to 5 produced 14% and 7 % increase in percentage metal removal at lower and higher initial concentration respectively.

4. Conclusions

The results of present study clearly show that ion exchange process is effective in removal of “Cu²⁺” and can provide solution for removal of such metals from acid mine drainage waste. Up to 64 and 28% metal removal could be achieved in 100 minute contact from aqueous solutions with initial concentrations 100 and 200 mg l⁻¹, respectively. For 100 mg l⁻¹ solution maximum “Cu²⁺” removal 64% achieved with 5 pH, 60 cm bed height and 5 LPH flow rate. Like wise for 200 mg l⁻¹ solution maximum “Cu²⁺” removal was achieved with 5 pH, 60 cm bed height and 5 LPH flow rate. The most significant effect was found to be pH. Then, resin bed height and

initial concentration of “Cu²⁺” interaction and pH–initial concentration of Cu(II) interaction were also found highly important.

5. Acknowledgements

The authors gratefully acknowledge the financial support from Board of Colleges and University Development, University of Pune, Pune. The authors also thank Pravara Rural Engineering College, Loni for kind support.

6. References

- [1] R. L. P. Kleinman, “Acid Mine Drainage, US Bureau of Mines Researches and Develops: Control Methods for Both Coal and Metal Mines,” *Environmental Science and Technology*, Vol. 24, No. 9, 1990, pp. 1278-1285.
- [2] A. Fyson, M. Kalin and L. W. Adrian, “Arsenic and Nickel Removal by Wetland Sediments,” *Proceedings of the International Land Reclamation and Mine Drainage Conference and 3rd International Conference on the Abatement of Acidic Drainage*, Pittsburgh, PA, Vol. 1, April 1994, pp. 109-118.
- [3] L. Clarke, “Coal Mining and Water Quality,” *Journal of Mines Metals and Fuels*, Vol. 44, 1996, pp. 181-183.
- [4] N. Kuyucak, Acid mine drainage prevention and control options. *CIM Bulletin* 95 (1060), 2002, pp. 96-102.
- [5] Filipek, L.H., Hatton, C., Gusek, J., Tsukamoto, T., Passive treatment of acid rock drainage (ARD): state of the practice. In: *Proceedings of the Tenth International Conference on Tailings and Mine Waste*, October, 2003, Colorado, USA, 2003, pp. 293-303.
- [6] Modis, K., Adam, K., Panagopoulos, K., Komtopoulos, A., Development and Validation of a geostatistical model for prediction of acid mine drainage in underground sulphide mines. *J. Trans. Instn. Min. Metall. (Sect A: Min. Industry)*, 1998, pp. A102-A107.
- [7] Gaikwad R.W. and Gupta D.V., Review On Removal Of Heavy Metals From Acid Mine Drainage, *Applied Ecology And Environmental Research* 6(3): 2008, pp. 79-96.
- [8] Kim, J. S., Chah, S. and Yi, J., “Preparation of Modified Silica for Heavy Metal Removal,” *Korean J. Chem. Eng.*, 17, 2000, pp. 118-121.
- [9] Kim, Y., Lee, B. and Yi, J., “Preparation of Functionalized Mesoporous Silica Containing Magnetite (MSM) for the Removal of Copper Ions in Aqueous Solutions and its Magnetic Separation,” *Separ. Sci. Technol.*, Vol. 38, 2003, pp. 2533-2548.
- [10] Lee, B., Kim, Y., Lee, H. and Yi, J., “Synthesis of Functionalized Porous Silicas via Templating Method as Heavy Metal Ion Adsorbents: The Introduction of Surface Hydrophilicity onto the Surface of Adsorbents,” *Micropor. Mesopor. Mat.*, 50(1), 2001, pp.77-90.
- [11] Kim, S. J., Lim, K. H., Joo, K.H., Lee, M. J., Kil, S.G. and Cho, S.Y., “Removal of Heavy Metal Cyanide Complexes by Ion Exchange,” *Korean J. Chem. Eng.*, 19(6), 2002, pp. 1078-1084.
- [12] Rengaraj, S. and Moon, S.H., “Kinetics of Adsorption of Co(II) Removal from Water and Wastewater by Ion Exchange Resins,” *Water Res.*, 36, 2002, pp. 1783-1793
- [13] Rengaraj, S., Joo, C., Kim, Y. and Yi, J., “Kinetics of Removal of Chromium from Water and Electronic Process Wastewater by Ion Exchange Resins: 1200H, 1500H and IRN97H,” *J. Hazard. Mater.*, B102, 2003, pp. 257-275.
- [14] M. E. R. Carmona, M. A. P. da Silva, S. G. Ferreira Leite, Biosorption of chromium using factorial experimental design, *Process Biochem.* 40, 2005, pp. 779-787.
- [15] K. Ravikumar, S. Krishnan, S. Ramalingam, K. Balu, Optimization of process variables by the application of response surface methodology for dye removal using a novel adsorbent, *Dyes Pigments* 72, 2007, pp. 66-75.
- [16] P.D. Berger, R.E. Maurer, *Experimental Design*, first ed., Easter Press Pvt. Ltd, Bangalore, India, 2002.