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Precipitation Conditions of Chevreul's Salt Using $(NH_4)_2SO_3$ from Synthetic Aqueous $CuSO_4$ Solutions

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In this study, synthetic aqueous $CuSO_4$ solution at a particular concentration was prepared. Chevreul's salt was precipitated using $(NH_4)_2SO_3$ solutions prepared at various concentrations. $(NH_4)_2SO_3$ solution was added drop by drop to the synthetic aqueous $CuSO_4$ solution. Chevreul's salt was characterised by XRD and SEM analysis. The effects of parameters such as $(NH_4)_2SO_3$ concentration, temperature, stirring speed and reaction time were investigated on precipitation of Chevreul's salt. 2^n factorial experimental design and orthogonal central composite design methods in the precipitation experiments were used. It was observed that the most effective parameters on the precipitation of Chevreul's salt were the temperature and the stirring speed. The obtained optimum conditions on maximum copper precipitation were: the $(NH_4)_2SO_3$ concentration 0.4 M, the temperature at 60 °C, the stirring speed was at 700 rpm and 15 min for reaction time. The chosen stationary parameters at the initial stage of the reaction were concentration of $CuSO_4$ solution 0.25 M and pH 4. Under these optimum conditions, the precipitated copper was 98.4 %.

Keywords: Chevreul's salt, Copper, Factorial experimental design, Orthogonal central composite experimental design.

INTRODUCTION

Copper is usually produced by cementation or electrowinning methods from solutions of soluble copper salts[1]. Precipitation of inorganic compounds from aqueous solutions generally are physical or chemical processes. Chemical processes can be various, like owing to hydrolytic action, ionic interaction or reduction. Precipitation of copper sulphites from aqueous solutions including copper is one of special importance in hydrometallurgical processes[2,3]. Chevreul's salt is known as a stable mixed-valence sulphite and attracts much interests due to its intense brick red colour as well as its highly stable mixed-valence state[4,5]. The precipitation of Chevreul's salt is a key stage in hydrometallurgical processes and very important in aqueous systems[6-8].

In recent years, studies of compounds of this type have been intensified. Chevreul's salt has been obtained using various methods and reagents[2,3]. Conklin and Hoffmann[9] have researched the metal ion-sulphur(IV) chemistry, thermodynamics and kinetics of transient iron(III)-sulphur(IV) complexes. Their measurements indicated that sulphite binds the metal through oxygen. Silva *et al.*[10] have examined synthesis, identification and thermal decomposition of double sulphites like $Cu_2SO_3.MSO_3.2H_2O$ (M=Cu, Fe, Mn or Cd). These salts have been obtained by saturation with sulphur dioxide gas from aqueous solutions of M(II) sulphates at room temperature. The thermal behaviour of double sulphites were estimated by thermogravimetry analysis and differential scanning calorimetric methods. They reported that these salt are thermally stable up to 200 °C and isostructural with Cu(II) replaced by Mn(II), Fe(II) and Cd(II) ions in $Cu_2SO_3{\cdot}MSO_3{\cdot}2H_2O$. Çolak *et al.*[11] obtained 99.78 % pure copper powder from Erzurum-Narman region oxidized copper containing 4.48 % Cu. They precipitated Chevreul's salt ($Cu_2SO_3.CuSO_3.2H_2O$) by using ammonia and sulphur dioxide. The best precipitation conditions of Chevreul's salt were found as pH: 4, the stirring speed: 600 rpm, the temperature: 60 °C, passing time SO_2: reaction time of 1 min after passing SO_2: 6 min. De Andrade *et al.*[12] have researched isomorphic series of double sulphites such as the $Cu_2SO_3.MSO_3.2H_2O$ (M=Cu, Fe, Mn or Cd) type. They found that the isomorphic Cu(II) in Chevreul's salt could be replaced by a divalent metal ion, forming an isomorphic series which properties are strongly dependent on the nature of M(II) cation. They determined that these mixed valence systems can be used as a model to identify intermediates under atmospheric conditions and to evaluate the role of transition metals as catalysts of S(IV) autoxidation in the conversion of SO_2 in the atmosphere, because of their interesting properties. Innoue *et al.*[13] salt synthesized Chevreul's by a reaction between $CuSO_4$ and $NaHSO_3$ and characterized by X-rays photoelectron spectroscopy, magnetic susceptibility, EPR and electronic spectroscopy. Parker and Muir[14] determined some conditions for precipitation of Chevreul's salt from impure leach solutions. They obtained 75 g of pure particulate copper per unit litre of solutions. Çalban *et al.*[15] researc-hed statistical modelling of Chevreul's salt recovery from leach solutions containing copper. They determined the optimum precipitation conditions of Chevreul's salt using leach solutions. They found as pH 3, temperature 62 °C, stirring speed 600 rpm, reaction time 12 min, SO_2 flow rate 358 L h^{-1} and concentration of $CuSO_4$ solution 7.383 gCu L^{-1}. Yesilyurt and Çalban[16] precipitated the Chevreul's salt from mixture of $CuSO_4$ and Na_2SO_3 solutions. They determined the optimum precipitation conditions as temperature 60 °C,

$[SO_3^{-2}]/[Cu^{+2}]$ ratio 1.6, pH 3, stirring speed 500 rpm and reaction time 20 min. Giovannelli *et al.*[17] researched an investigation into the surface layers formed on oxidized copper exposed to SO_2 in humid air under hypoxic conditions. Chevreul's salt exhibited orthorhombic symmetry at room temperature. A mechanistic analogy with bronze disease of archaeological artefacts has been indicated.

The aim of this study was to precipitate Chevreul's salt using $(NH_4)_2SO_3$ solutions at various concentrations from synthetic aqueous $CuSO_4$ solutions. 2^n factorial and orthogonal central composite experimental design methods in the precipitation experiments have used to determine the optimum conditions.

EXPERIMENTAL

Experimental design is widely used for controlling the effects of parameters in many processes. Its usage decreases the number of experiments, using time and the quantity of materials used. Furthermore, analysis based on the results is easily carried out and experimental errors are minimised. Statistical methods measure the effects of change in operating variables and their interactions on the process through factorial experimental designs. Today, the most widely used experimental design to estimate main effects, intercalarily interaction effects is the 2^n factorial design. According to the 2^n factorial experimental design method, the principal steps of experiments are designed: determination of response variables, choice of factor levels and statistical analysis of the data. Consequently, the final step of the work is to obtain a statistical regression model[18]. A factor is any aspect of experimental conditions affecting the results of experiments. A two-level experimental design requires 2^n runs for two levels of each factor. Coded values of variables are high level = +1 and low level = -1. The centre coordinates are zero between factor levels and this value coincides with the origin of coordinates.

The variance analysis tables (ANOVA) show the effects of all variables and their mutual interactions[19,20]. Experimental data based on the design is fitted to a second-order polynomial equation as follows.

$$\hat{Y} = b_0 + \sum_{i=1}^{n} b_i X_i + \sum_{i=1}^{n} b_{ii}(X_1^2 - \bar{X}_i^2) + \sum_{i=1}^{n}\sum_{j=1}^{n} b_{ij} X_i X_j \quad (1)$$

where, the coefficient b_i shows the main effects of the factors X_i; b_{ii} and b_{ij} coefficients represent second-order interaction terms. The independent term b_0 represents the response at the zero level of every factor ($X_1 = X_2 = X_3 = X_i = 0$).

The main effects and interactions obtained from regression model are entirely half values obtained from the Yates algoritm. This is because of the response over two levels of each independent variable (from -1 to +1)[21,22].

Second-order effects cannot be estimated by 2^n factorial designs. If the variance analysis indicates that second-order effects are significant, auxiliary experiments are carried out. Among various second-order designs, the orthogonal central composite design is the most popular which requires 2^n auxiliary runs conducted at two new factor levels, -β, + β. They are calculated by the following relation:

$$\beta = \left(\frac{QF}{4}\right)^{1/4} \quad (2)$$

$$Q = [(N)^{1/2} - (F)^{1/2}]^2 \quad (3)$$

$$N = 2n + F + M_0 \quad (4)$$

where F is the number of experiments in the factorial design, N is the total number of experiments and m_0 is the number of central replicates.

In the planning of experimental designs, coded values are usually used instead of absolute values of the variables. The relationship between coded value (X) and absolute value (Z) is as follows:

$$X = \frac{2(Z - Z_0)}{(Z_2 - Z_1)} \quad (5)$$

where Z_1 is the low level, Z_2 is the high level and Z_0 is the medium level of the variable[19,20,23,24].

Precipitation process of Chevreul's salt was carried out in a glass reactor (500 mL) with three necks. A synthetic aqueous 0.25 M $CuSO_4$ solution was put into the reactor. The reactor was submerged in a Memmert™ water bath with a digital temperature controller and the contents of the reactor were stirred with a Yellow Line™ mechanical stirrer. The probe of a WTW™ pH meter, which simultaneously measures pH and temperature, was immersed in the solution. The reactor was fitted with a back-cooler to prevent losses by evaporation process. When the contents of the reactor reached the desired temperature, stirring was started at a stable speed. While the reactor content was being stirred, $(NH_4)_2SO_3$ solution at various concentrations was added drop by drop.

The stirring continued during the reaction time. At the end of the reaction period, the precipitate was immediately filtered through a Filtrak 389 and was washed with deionised water. The precipitate was air-dried. Identification of the precipitate with intense brick-red colour was made by X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). X-ray and SEM results of the precipitate are demonstrated respectively in Figs. 1 and 2. The copper amounts in the precipitate and the filtrate were determined complexometrically[25]. The factorial experimental design and the orthogonal central composite design methods were used to determine the experimental plan.

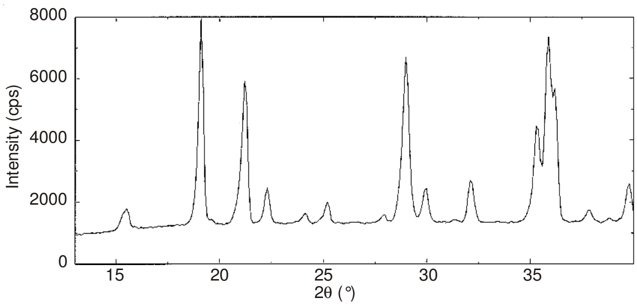

Fig. 1. XRD of Chevreul's salt

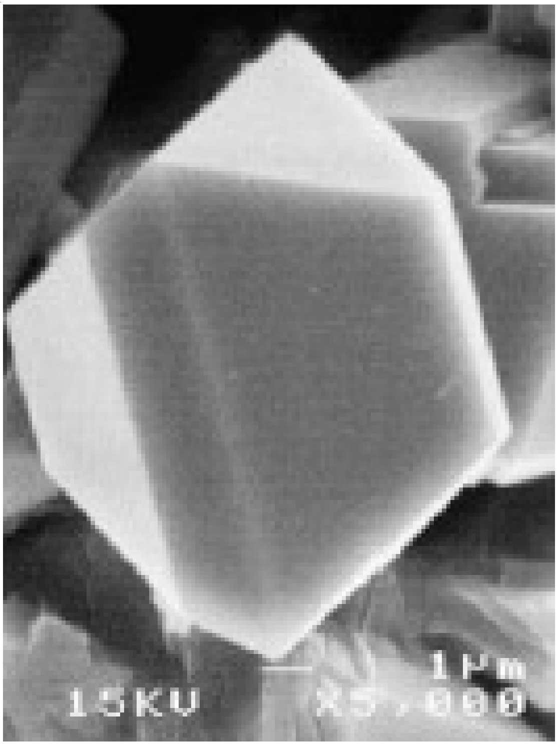

Fig. 2. SEM of Chevreul's salt

RESULTS AND DISCUSSION

Precipitation of Chevreul's salt: When Chevreul's salt is precipitated from synthetic aqueous $CuSO_4$ solution, the reactions taking place in the medium can be written as follows[14,19,26]:

$$3CuSO_{4(aq)} + 3(NH_4)_2SO_{3(aq)} \rightarrow 3(NH_4)_2SO_4(aq) + Cu_2SO_3.CuSO_3.2H_2O(s) + H_2SO_4(aq) \quad (6)$$

Effects of parameters on precipitation of Chevreul's salt: Effects of the parameters on Chevreul's salt precipitation were investigated for parameters using the values given in Table-1.

TABLE-1
FACTOR LEVELS ON THE PRECIPITATION OF CHEVREUL'S SALT

Factors	Low level (-)	High level (+)	Medium level (0)
X_1: $(NH_4)_2SO_3$ Concentration (M)	0.3	0.4	0.35
X_2: Temperature (°C)	60	70	65
X_3: Stirring speed (rpm)	600	700	650
X_4: Reaction time (min.)	15	20	17.5

Effect of solution concentration was investigated by experiments using a constant solution concentration of 0.25 M. Extremely pure Chevreul's salt was precipitated from these synthetic aqueous $CuSO_4$ solutions using $(NH_4)_2SO_3$ solution at various concentrations. In all experiments, the temperature, the stirring speed, the $(NH_4)_2SO_3$ solution and the pH were meticulously controlled during the reaction. All the results are presented in Tables 2-4. As seen from the tables, the effect of solution concentration on the precipitate amount was very small for the chosen diluted or concentrated solutions.

Effect of concentration was researched in the range of 0.27-0.43 M. Chevreul's salt was precipitated in pure form from the reaction. The obtained Chevreul's salt amounts which are using central values of the other parameters for 0.27, 0.35

TABLE-2
(2^4) FACTORIAL EXPERIMENTAL DESIGN MATRIX

Exp. No.	X_1	X_2	X_3	X_4	Y_e (%)	$\hat{Y}_i$ (Model)	e_i: $Y_e - \hat{Y}_i$
1	-	-	-	-	91.90	90.07	1.83
2	-	-	-	+	90.60	90.93	-0.33
3	-	-	+	-	92.10	93.50	-1.40
4	-	-	+	+	92.00	90.91	1.09
5	-	+	-	-	93.90	94.49	-0.59
6	-	+	-	+	94.90	95.35	-0.45
7	-	+	+	-	96.50	95.92	0.58
8	-	+	+	+	94.20	93.33	0.87
9	+	-	-	-	89.80	90.31	-0.51
10	+	-	-	+	91.10	91.18	-0.08
11	+	-	+	-	98.40	95.39	3.01
12	+	-	+	+	91.70	92.81	-1.11
13	+	+	-	-	94.00	93.58	0.42
14	+	+	-	+	95.20	94.45	0.75
15	+	+	+	-	96.30	96.66	-0.36
16	+	+	+	+	93.80	94.08	-0.28
1	0	0	0	0	90.40	-	-
2	0	0	0	0	90.70	-	-
3	0	0	0	0	90.20	-	-

and 0.43 M concentrations were 92.30, 90.43 (the mean value of three central replications) and 92.90 %, respectively. The results obtained from experiments are presented in Tables 2, 5 and Fig. 3. As seen from the Tables and the Fig. 3 the obtained results in three different concentrations were almost identical. The change in precipitated copper percentage was very low and could be neglected and for that reason, the effect of concentration is minimal on the precipitated copper amount.

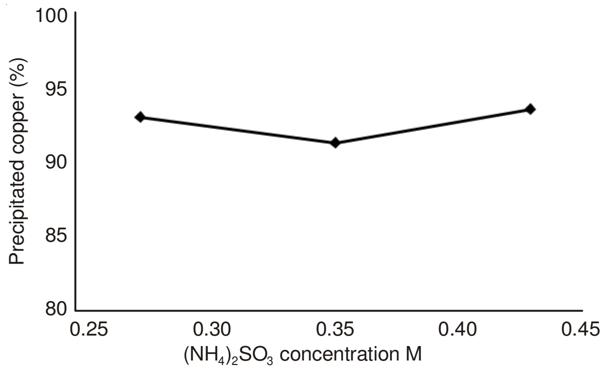

Fig. 3. Effect of $(NH_4)_2SO_3$ concentration on the precipitation of Chevreul's salt using central values of the other parameters

Effect of temperature was researched in the range of 57-73 °C. The obtained precipitated amounts which are using central values of the other parameters for 57, 65 and 73 °C temperatures were 87.60, 90.43 (the mean value of three central replications) and 93 %, respectively. The results obtained from experiments are presented in Tables 2, 5 and Fig. 4. As seen from the Tables and Fig. 4, Chevreul's salt amounts increased with increasing the reaction temperature.

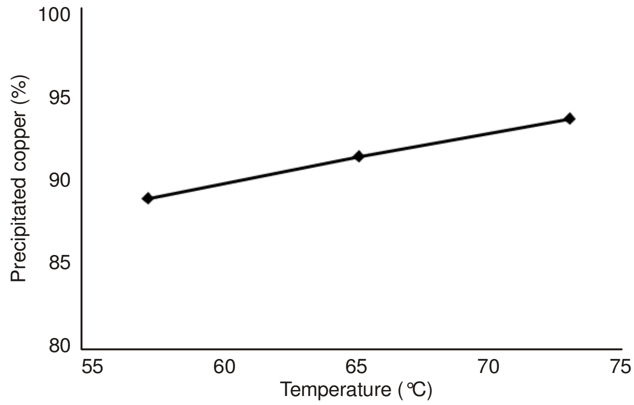

Fig. 4. Effect of temperature on the precipitation of Chevreul's salt using central values of the other parameters

Effect of the stirring speed was researched in the range of 570-730 rpm. The obtained precipitated amounts which are using central values of the other parameters for 570, 650 and 730 rpm stirring speeds were 89.80, 90.43 (the mean value of three central replications) and 91.30 %, respectively. The obtained results from experiments are presented in Tables 2 & 5; and Fig. 5. As seen from the Tables and Fig. 5, Chevreul's salt slightly increased with increasing the stirring speed.

Effect of reaction time was studied in the range of 13.63-21.37 min. The obtained copper amounts which are using central values of the other parameters for 13.63, 17.5 and 21.37 min were 90.90, 90.43 (the mean value of three central replications) and 91.20 %, respectively. The obtained results from experiments were given in Tables 2, 5 and Fig. 6. As seen from the Tables and Fig. 6, the percentage of precipitated

TABLE-3
TABLE OF VARIANCE ANALYSIS (ANOVA)

Source of variation	Sum of squares	df	Mean squares	F_o Ratio	Decision (α = 0.05)	Decision (α = 0.01)
X_1: $(NH_4)_2SO_3$ Concentration (M)	0	1	0	0	Ineffective	Ineffective
X_2: Temperature (°C)	40	1	40	315.71	Effective	Effective
X_3: Stirring speed (rpm)	10	1	10	78.93	Effective	Ineffective
X_4: Reaction time (min.)	0	1	0	0	Ineffective	Ineffective
$LOF_{curvature}$	24.2	1	24.2	191	Effective	Effective
Model lack of fit	77.39	11	7.04	610.81	Effective	Effective
Experimental error	0.13	2	0.06	-	-	-
Total	151.72	18	-	-	-	-

$F_{0.95;1;2} = 18.51$ $F_{0.99;1;2} = 98.50$ $F_{0.95;11;2} = 19.40$ $F_{0.99;11;2} = 99.40$

TABLE-4
TABLE OF VARIANCE ANALYSIS FOR THE SECOND ORDER MODEL

Source of variation	Sum of squares	df	Mean squares	F_o Ratio	Decision (α = 0.01)	Decision (α = 0.05)
X_1	0	1	0	0	Ineffective	Ineffective
X_2	40	1	40	315.71	Effective	Effective
X_3	10	1	10	78.93	Ineffective	Effective
X_4	0	1	0	0	Ineffective	Ineffective
X_1^2	30	1	30	236.78	Effective	Effective
X_2^2	0	1	0	0	Ineffective	Ineffective
X_3^2	10	1	10	78.93	Ineffective	Effective
X_4^2	10	1	10	78.93	Ineffective	Effective
X_3X_4	10	1	10	78.93	Ineffective	Effective
$LOF_{curvature}$	24.2	1	24.2	191	Effective	Effective
Model lack of fit	17.39	9	1.93	15.25	Effective	Ineffective
Experimental error	0.13	2	0.06	-	-	-
Total	151.72	26	-	-	-	-

$F_{0.99;1;2} = 98.5$ $F_{0.99;9;2} = 99.39$ $F_{0.95;1;2} = 18.53$ $F_{0.95;9;2} = 19.38$

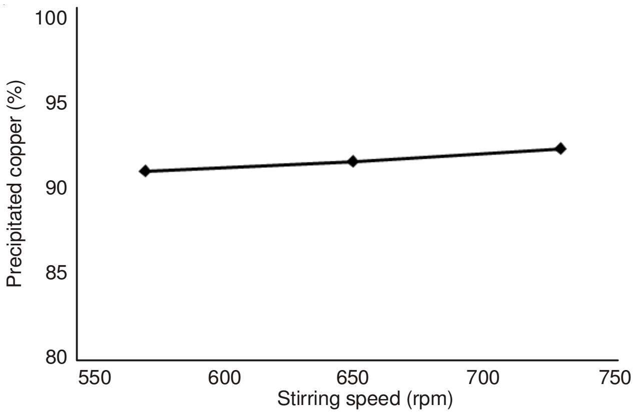

Fig. 5. Effect of stirring speed on the precipitation of Chevreul's salt using central values of the other parameters

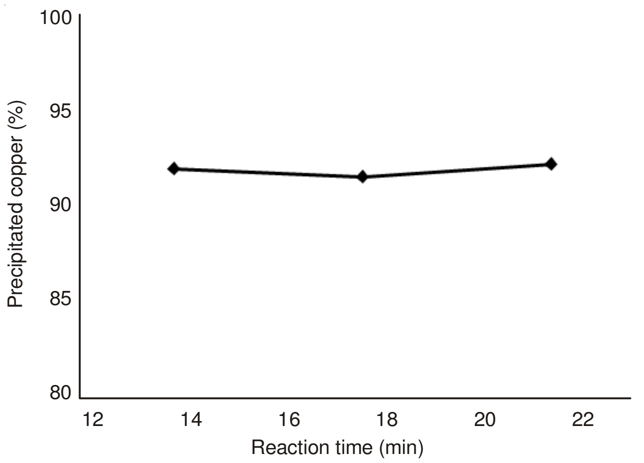

Fig. 6. Effect of reaction time on the precipitation of Chevreul's salt using central values of the other parameters

copper is independent on reaction time among 13.63 and 21.37 min.

Statistical analysis of Chevreul's salt precipitation: Precipitation tests of Chevreul's salt with ammonium sulphite were carried out. The collected data was analysed by ANOVA using the MATLAB computer software package for the evaluation of the effect of each parameter on the optimization criteria. In light of pre-experiments, $CuSO_4$ concentration and reaction pH, were maintained as constant parameters. Other factors such as the $(NH_4)_2SO_3$ concentration, the temperature, the stirring speed and the reaction time were chosen as independent variables and their high and low levels were decided as shown in Table. First, a first-order model was chosen to fit the experiment data:1

TABLE-6.
FACTOR LEVELS FOR THE SECOND ORDER MODEL

Factors	Low Level (-)	High Level (+)	Medium Level (0)
X_1: $(NH_4)_2SO_3$ Concentration (M)	– 0.27	– 0.43	0.35
X_2: Temperature (ºC)	57	73	65
X_3: Stirring speed (rpm)	570	730	650
X_4: Reaction time min.)	– 13.63	– 21.37	17.5

$$\hat{Y} = b_o + \sum_{n=1}^{4} b_i X_i + \sum_{i=1}^{n}\sum_{j>1}^{n} b_{ij} X_i X_j \quad (7)$$

With four factors, 2^4 full factorial design requires 16 runs. Furthermore, three central replications were added to the experimental plan in order to estimate pure experimental error. The results are given in Table-2. To test the significance of the factor effects, an analysis of variance was conducted at 95 and 99 % confidence intervals. The results are shown in Tables 3 and 4. At both confidence intervals, the $(NH_4)_2SO_3$ concentration (X_1) and the reaction time (X_4) range have been found to be insignificant. Furthermore, the effects of pure quadratic terms were controlled by means of the following statistic:

$$LOF_{curv.} = \frac{m_o F(\bar{Y}_1 - \bar{Y}_0)^2}{m_o + F} \quad (8)$$

where m_o is the number of central point experiments, F is the number of factorial experiments, $\bar{Y}_1$ is the mean of factorial experiments and $\bar{Y}_0$ is the mean of central replicates.

As seen from Tables 3 and 4, results of variance analysis showed a curvature effect. According to these results, the regression model was obtained as follows.

Copper precipitated as Chevreul's salt from $CuSO_4$ solution ($\bar{Y}_e$), (%):

$$\bar{Y}_e = 89.6604 + 1.4218 X_2 + 0.7660 X_3 + 1.5284 X_1^2 + 0.6715 X_3^2 + 0.8805 X_4^2 - 0.8625 X_3X_4$$
(at 95 and 99 % confidence intervals) (effective model) (9)

According to the results of variance analysis, quadratic terms are effective. Therefore, the orthogonal central composite design was planned to estimate quadratic terms. With F = 16, m_0 = 3 and n = 4, β is calculated as 1.547 according to eqn. (2). Factor levels for second-order model are given in Tables 5 and 6. Also, the second-order model is defined as in eqns. (1) and (10):

$$\bar{X}_i^2 = \frac{1}{N}\sum_{i}^{N} X_i^2 = \frac{F + 2\beta^2}{N} \quad (10)$$

TABLE-5
EXPERIMENTAL DESIGN MATRIX FOR THE SECOND ORDER MODEL

Exp. No.	X_1	X_2	X_3	X_4	Precipitate amounts (%)
20	-1.547	0	0	0	92.30
21	+1.547	0	0	0	92.90
22	0	-1.547	0	0	87.60
23	0	+1.547	0	0	93.00
24	0	0	-1.547	0	89.80
25	0	0	+1.547	0	91.30
26	0	0	0	-1.547	90.90
27	0	0	0	+1.547	91.20

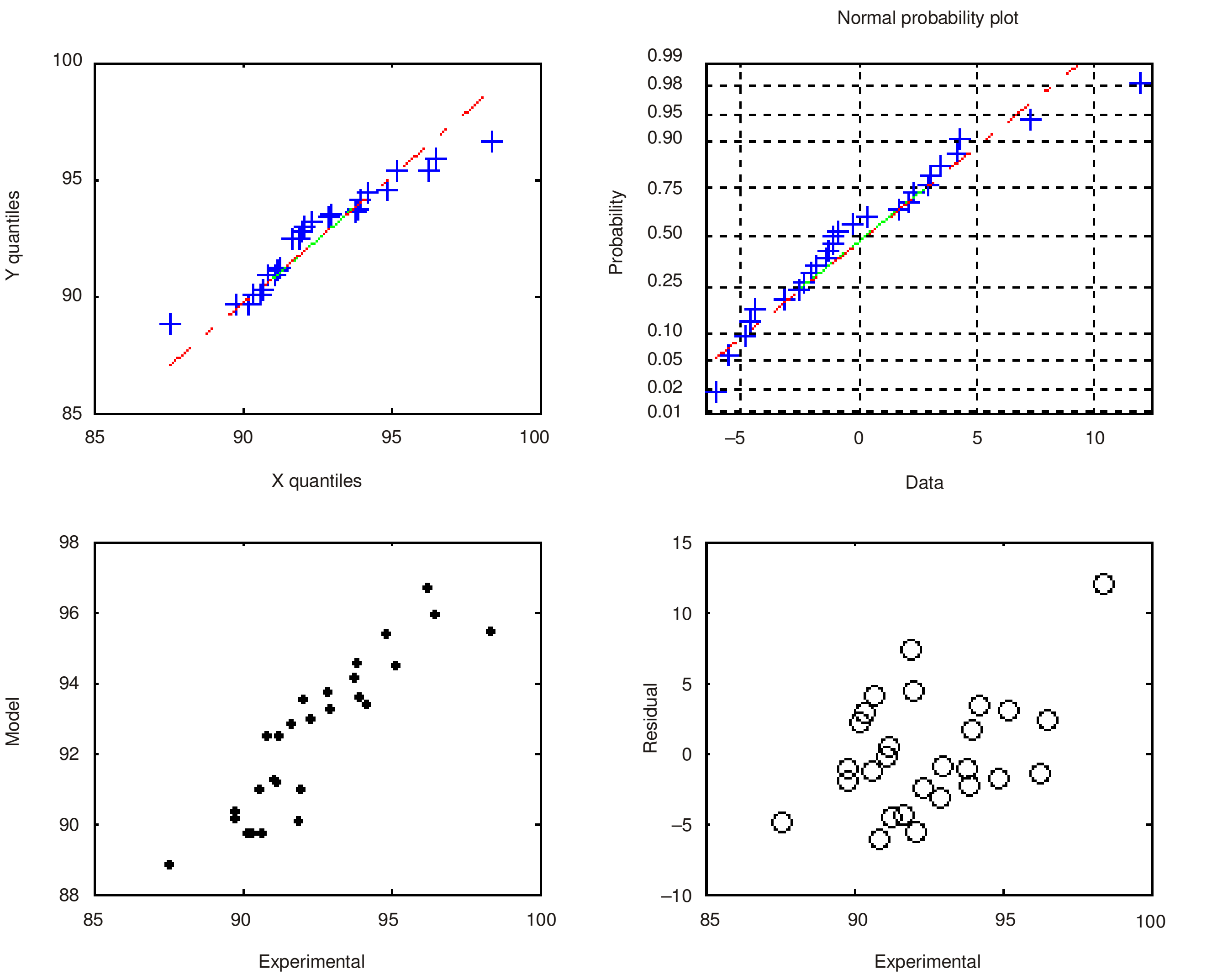

Fig. 7. Statistical test graphs

The full second-order model obtained by regression analysis is as follows:

$$\overline{Y}_e = 89.6604 + 0.2467\,X_1 + 1.4218\,X_2 + 0.7660\,X_3\,0.4299\,X_4 + 1.5284\,X_1^2 + 0.5670\,X_2^2 + 0.6715\,X_3^2 + 0.8805\,X_4^2 - 0.2875\,X_1X_2 + 0.4125\,X_1X_3 - 0.2500\,X_1X_4 - 0.5000\,X_2X_3 + 0.2625\,X_2X_4 - 0.8625\,X_3X_4 \quad (11)$$

The ANOVA of obtained results shows that all of the variables studied and their combinations affect Chevreul's salt recovery from synthetic aqueous solutions. As seen from Tables 3 and 4, the temperature, the stirring speed and interactions of the stirring speed with reaction time are effective on precipitation of Chevreul's salt. Conversely, the ANOVA results show that reaction time and the $(NH_4)_2SO_3$ concentration have no effect on Chevreul's salt recovery.

Systematic errors in a well-established model are absent. Normalised residuals depend on experimental errors and these values exhibit a normal distribution. The tests'graphs are shown in Fig. 7.

Conclusions

- The use of ammonium sulphite in the process facilitates the precipitate of Chevreul's salt from solutions containing copper.
- After Chevreul's salt is filtrated, ammonium sulphate can be obtained from the remaining solution. Waste ammonium sulphate solution can be used in fertilizer production.
- The sulphuric acid produced during reaction dissolves Chevreul's salt and decreases the amount of precipitated Chevreul's salt. Therefore, the reaction time has been selected as short.
- After evaporation of sulphuric acid solution, condensed solution can be used in the production of sulphuric acid solution.
- Although ammonium sulphite is expensive, the products obtained at the end of the reaction are more valuable.
- The most effective parameters on Chevreul's salt precipitation have been found as the temperature and the stirring speed. However, the ammonium sulphite concentration and the reaction time have no effect in the chosen range.
- The optimum conditions obtained on maximum copper precipitation were: the $(NH_4)_2SO_3$ concentration 0.4 M, the temperature 60 °C, the stirring speed 700 rpm and reaction time of 15 min. The stationary parameters chosen at the initial stage of the reaction were; concentration of $CuSO_4$ solution 0.25 M and pH 4.
- Under optimum conditions, precipitated copper was 98.4 %.

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