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Optimization of Microwave Roasting for Dechlorination of CuCl Residue from Zinc Hydrometallurgy

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ABSTRACT

Removal of chlorine (Cl) from the CuCl residue in the process of zinc hydrometallurgy is of great importance to improve the process economics. The current processing methods result in generation of large quantities of polluted discharge necessitating waste treatment systems. The present work attempts to de-chlorinate the CuCl residue through thermal treatment with the application of microwave energy. Relationship between explanatory and response variables was explored by response surface methodology (RSM) technique searching to optimize the dechlorination efficiency. The effect of three major parameters such as temperature, duration of heating, and particle size of samples were assessed and the optimal process conditions were identified. Analysis of variance (ANOVA) was utilized to identify the suitable model and to eliminate the insignificant model parameters. The optimized process conditions for maximizing the dechlorination efficiency are identified to be a roasting temperature of 426 °C, heating time 125 min, and particle size of samples 0.12 mm. A dechlorination efficiency of 93% could be achieved at the optimal process conditions, and validated through repeat experimental runs at the optimized process conditions. The optimized process samples are characterized utilizing XRD and SEM/EDS to validate the dechlorination efficiency.

KEYWORDS: Microwave roasting, zinc hydrometallurgy, CuCl residue, dechlorination, response surface methodology.

INTRODUCTION

Accumulation of chlorine (Cl) in the process of Zn manufacturing is of serious concern, since a concentration in excess of 100 mg/L during the process of electrolysis will affect the stability of electro deposition process [Mathewson C. H, 1959]. It would accelerate the consumption of cathode, anode and elevate the power consumption in addition to causing serious corrosion to the container [Güresin N. and Topkaya Y. A., 1998; Jha M. K. et al., 2001]. Hence, removal of chlorine is imperative to improve the economics of the process and it is important that chlorine is removed before the electro deposition. Currently, the removal of chlorine is facilitated either by roasting the raw material [Toshihiko S, 1998; Yamamoto Y. and Sato K., 1998], or by the removal of chlorine (Cl^-) from zinc sulfate solution through addition of Cu^+ to form CuCl. Removal through addition of Cu^+ is the popular method commercially due to the high rate of removal and low cost. However, the CuCl residue needs to be further treated for safe disposal, then it is washed with an alkaline solution, such as Na_2CO_3, wherein CuCl turns into a NaCl solution before being discharged.

Microwave irradiation has been widely investigated due to its capability to heat materials at molecular level, which leads to homogeneous and quick thermal heating [Hidaka H. et al., 2007; Guo S. et al., 2009; Uysal N., et al., 2009; Isabel S. S. P. and Helena M. V. M. S., 2012; Swart A. J. and Mendonidis P., 2013]. Compared with traditional heating techniques, microwave heating provides additional advantages such as higher heating rates, selective heating, precise control of temperature, small equipment size and reduced waste [Jones D. A. et al., 2002].

The application of microwave heating for de-chlorination of the CuCl residue is explored in the present work. In order for this process to be effective, a high rate of the removal of chlorine is desirable and hence a process optimization exercise to identify the optimum conditions is performed. The processing variables explored were the roasting temperature, duration of heating and particle size, while the response variable was the dechlorination rate [Talip K., 2008; Liu J. et al., 2013; Yang K. et al., 2013]. The relationship between the processing variables and the response variable was determined by the response surface methodology (RSM) that has been reported as a highly technique for aiding in multivariable experimental design, statistical modeling and process optimization [Duan X. et al., 2011; Chen G. et al., 2012]. It is the most economical and convenient method for characterizing a complicated experimental process [Zhang Z. et al., 2009] with minimum number of experiments [Ahmad A. L. et al., 2009; Shweta S. et al., 2009].

The structural change of residue due to the dechlorination process is investigated by means of XRD and SEM/EDS.

EXPERIMENTAL

Materials

The CuCl residue cake was supplied by a zinc hydrometallurgy smelter in Yunnan Province, China. The main chemical composition of CuCl residue after drying at 100 °C for 12 h is shown in Table I. The Cl content of the dried CuCl residue is found to be 16.76%.

As seen in Figure 1, the main phases of sample are Cu_2O and CuCl. Figure 2 shows the response of the sample in terms of increase in temperature with respect to time, exposed to a microwave power of 1.28 kW, on a sample of 100 g. An exponential increase in temperature beyond 8 minutes was observed, with the resultant temperature of 600 ºC achieved in a duration of less

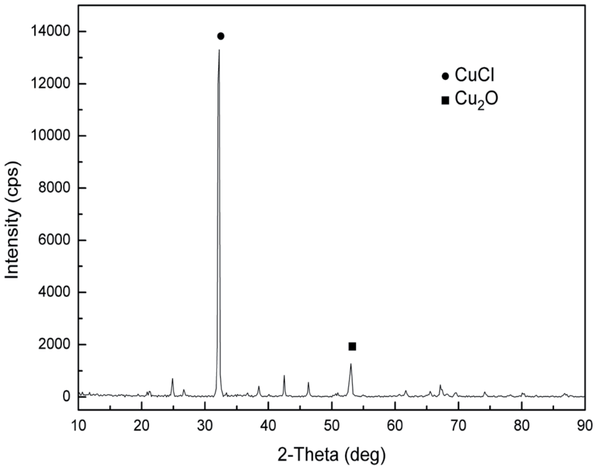


Figure 1. XRD patterns of the raw materials.

Table I. The Chemical Composition of CuCl residue.

Composition	Cu	Cl	O	S	Zn	Fe	Ca
Content (mass%)	49.98	16.76	27.21	3.30	1.99	0.39	0.37

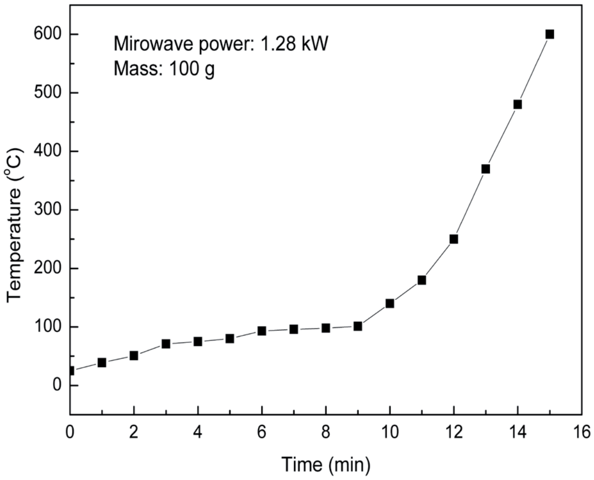


Figure 2. The heating curve of CuCl residue under microwave irradiation (microwave power density: 1.28 kW/100 g).

than 15 minutes. The favorable microwave absorbance characteristics of the CuCl compound is evidence based on Figure 2.

Experimental device

Roasting experiments were carried out using a microwave reactor system (2.45 GHz), which utilizes a single-mode continuous controllable power up to 3 kW (Figure 3). The dried and grinded samples were placed in a well-insulated mullite crucible to minimize the heat loss. The stirring system was fixed directly above the crucible and off-gases were removed through a suction arrangement passing through an absorption system.

Design of experiments

A central composite design (CCD) of RSM is utilized to identify the optimal experimental conditions to maximize the de-chlorination with a minimum number of experiments and to identify the significant parameters, as well as the interactions between them. A total of 20 experiments, including 6 repetition runs at the center point of all the variables, were performed. The dependant variables selected are temperature (χ_1), exposition time (χ_2) and particle size of samples (χ_3). The range of process parameters investigated in the present work, denoted in the form of coded variables is shown in Table II, while the exact experimental conditions are shown in Table III. The ranges of these variables are selected through rigorous literature analysis as well

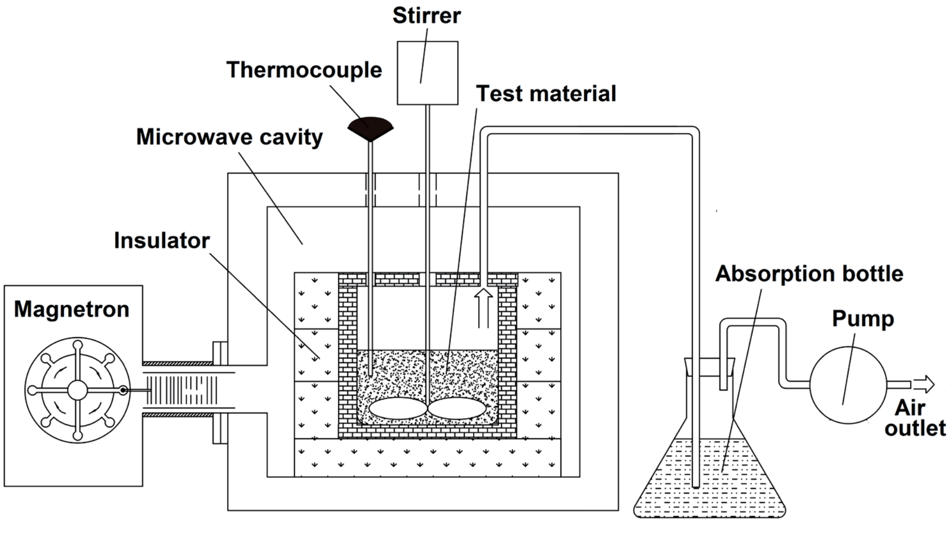


Figure 3. Scheme of the microwave reactor system.

Table II. Range of variables utilized in the experimental design.

Variables	Coded variable level				
	-1.682	-1	0	1	1.682
Temperature (°C)	231.82	300	400	500	568.18
Exposition time (min)	86.36	100	120	140	153.64
Particle size (mm)	0.09	0.10	0.13	0.15	0.16

as through the results of the preliminary experiments.

The mathematical model relating the independent variable to the dependent variable is developed through the model equation as shown below,

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i \chi_i + \sum_{i=1}^{k} \beta_{ii} \chi_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \beta_{ij} \chi_i \chi_j \quad (1)$$

where Y is the dependent response, β_0 is the constant coefficient, β_i is the linear coefficient, β_{ii} is the quadratic coefficients and β_{ij} is the interaction coefficients, k is the number of factors studied and optimized in the experiment, χ_i, χ_j are the coded values of independent variables, and the terms $\chi_i\chi_j$ and χ_i^2 represent the interaction and quadratic terms, respectively.

The experimental data are analyzed using statistical software Design Expert version 7.1.5 (STAT-EASE Inc., Minneapolis, USA). The optimum conditions are identified by maximizing the objective function through the model equation developed. Three dimensional response surface plots indicating the effect of independent variables on the dependent variables are developed.

RESULTS AND DISCUSSION

The experimental conditions along with the results are shown in Table III. The yield is observed to vary in the range of 51.29% to 92.89%. The repeat runs at the center point of the variables (experiment runs 15-20) indicate the uncertainties involved in the experimental system.

Model Development

Table IV presents the results of various models tested with the experimental data.

Table III. Central composite design arrangement and results.

Run	χ_1 (°C)	χ_2 (min)	χ_3 (mm)	Y (%)
1	300.00	100.00	0.10	77.47
2	500.00	100.00	0.10	90.14
3	300.00	140.00	0.10	79.17
4	500.00	140.00	0.10	91.96
5	300.00	100.00	0.15	70.23
6	500.00	100.00	0.15	77.68
7	300.00	140.00	0.15	73.28
8	500.00	140.00	0.15	89.55
9	231.82	120.00	0.13	51.29
10	568.18	120.00	0.13	92.26
11	400.00	86.36	0.13	74.67
12	400.00	153.64	0.13	91.79
13	400.00	120.00	0.09	92.89
14	400.00	120.00	0.16	78.97
15	400.00	120.00	0.13	90.15
16	400.00	120.00	0.13	91.13
17	400.00	120.00	0.13	90.67
18	400.00	120.00	0.13	90.58
19	400.00	120.00	0.13	90.78
20	400.00	120.00	0.13	91.32

A high F value coupled with the low P value indicates the suitability of the model. Based on the results in Table IV the cubic model is eliminated at a statistical level significance of 0.05. As suggested by the software the quadratic model is found to be the most suitable model relating dependent and independent variables. Several indicators were used to evaluate the adequacy of the fitted model and the results are shown in Table V. The coefficient of determination (R^2), the adjusted determination coefficient (adj. R^2), coefficients of variation (CV) and model significance (F-value) are used to judge the adequacy of the model.

Table IV. Statistical parameters for sequential models.

Source	Sum of squares	Degree of Freedom	Mean square	F-value	p-value	R-Squared
Linear	828.99	11	75.36	436.79	<0.0001	0.6241
2FI	702.37	8	100.30	581.31	<0.0001	0.6362
Quadratic	164.38	5	32.84	190.54	<0.0001	0.9252
Pure Error	0.86	5	0.17			

As shown in Table V, the model F-value of 13.73 implies that model is significant. There is only a 0.02% chance that Model F-value this large could occur because of noise. P-value less than 0.0001 shows that model terms are significant. The accuracy and variability of the above model could be evaluated by the coefficient of determination R^2. The coefficient of determination (R^2) of the model is obtained 0.9252, which indicates that 92.52% of the variability in the dependent variable could be explained, and only 7.48% of the total variations cannot be explained by the model. Additionally, the value of adjusted determination coefficient (adj. R^2) is 0.8578, suggests good correlations between the dependent and independent variables. CV is the ratio of the standard error of estimate to the mean value of the observed response, expressed in percent. A model can be considered reasonably reproducible if the CV is not greater than 10%. A low value of CV (4.85%) shows the high degree of precision and a reliability of the experimental values [Chen G. et al., 2012].

Based on the F-value (Table V), χ_1 shows the largest F-value of 61.79, indicating that temperature had the most significant effect on dechlorination efficiency of the CuCl residue, compared to χ_2 and χ_3. The effect of duration on dechlorination is more significant than particle size, with F-values being 9.89 and 11.71 respectively.

By applying the least squares method and multiple regression analysis on the experimental results, the following cubic equation is found to relate the dependent variable after eliminating the in-significant

Table V. Analysis of variance (ANOVA) for response surface cubic model for dechlorination.

Source	Sum of squares	Degree of freedom	Mean square	F-value	p-value
Model	2042.49	9	226.94	13.73	0.0002
χ_1	1021.00	1	1021.00	61.79	< 0.0001
χ_2	163.35	1	163.35	9.89	0.0104
χ_3	193.53	1	193.53	11.71	0.0065
$\chi_1\chi_2$	9.99	1	9.99	0.60	0.4548
$\chi_1\chi_3$	0.38	1	0.38	0.023	0.8827
$\chi_2\chi_3$	16.25	1	16.25	0.98	0.3448
χ_1^2	589.94	1	589.94	35.70	0.0001
χ_2^2	79.46	1	79.46	4.81	0.0531
χ_3^2	27.99	1	27.99	1.69	0.2223
Residual	165.24	10	16.52		
Pure Error	0.86	5	0.17		
Cor Total	2207.73	19			

R^2=0.9252; adj. R^2=0.8578; CV=4.85%.

parameters as shown in Equation (2):

$$Y = 90.72 + 8.65\chi_1 + 3.46\chi_2 - 3.76\chi_3 - 6.40\chi_1^2 - 2.35\chi_2^2 \quad (2)$$

where and Y is dechlorination efficiency (%). The suitability of model equation is evaluated using the correlation coefficients (R^2), which is 0.9252 for Equation (2). The R^2 value of the model equation is high which indicates a good agreement between experimental data and the model prediction.

The predicted values of dechlorination efficiency are calculated using the regression model and compared with experimental data in Figure 4. As can be seen, the predicted values are close to the experimental data, indicating the suitability of the model for optimization of dechlorination of the CuCl residue.

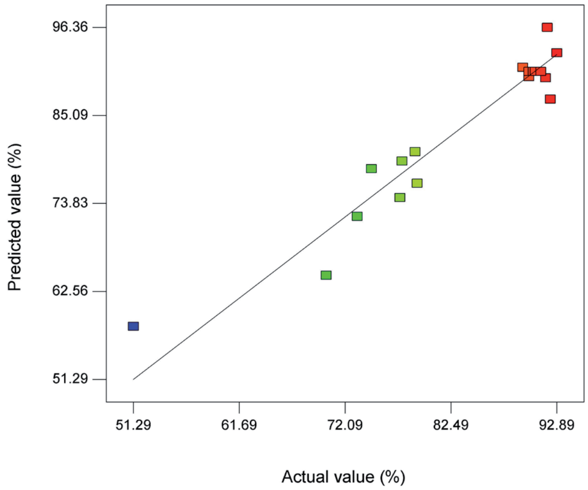


Figure 4. Linear correlation between actual and predicted values.

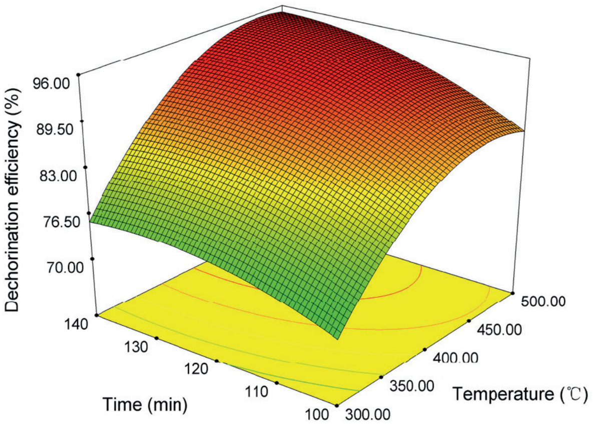


Figure 5. Three-dimensional response surface and contour plot of temperature vs. time on dechlorination efficiency.

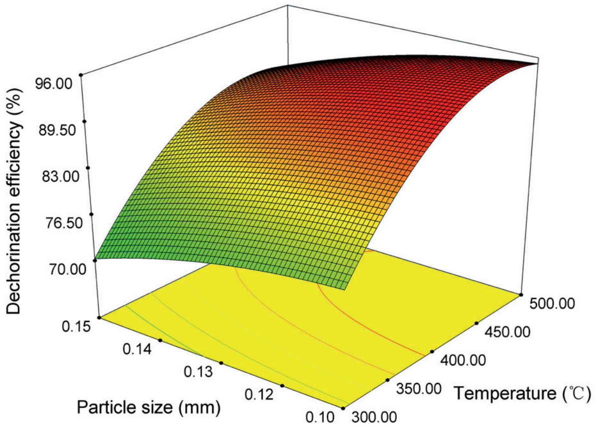


Figure 6. Three-dimensional response surface and contour plot of temperature vs. particle size on dechlorination efficiency.

Interactions of the factors

The dechlorination efficiency of CuCl residue over different combinations of independent variables can be visualized through the following plots. Figure 5 shows the effect of roasting temperature and exposition time on dechlorination of CuCl residue (particle size is 0.12 mm), while Figure 6 shows the effect of roasting temperature and particle size of samples (exposition time is 125.33 min). It can be seen from Figures 5 and 6 that dechlorination peaks at a temperature of around 430 °C. The rate of dechlorination is found to be reduced, reaching an asymptote at temperatures in excess of 430 °C. An increase in temperature would increase the rate of decomposition and hence an increase in the dechlorination efficiency with increase in temperature is observed. However, the due to the lack of oxidant (steam or air) the rate of decomposition is reduced. Besides this condition, the samples are melted because the melting point of CuCl is 430 °C, but they are highly viscous, which also affects negatively the rate of decomposition. Although the rate of dechlorination decreases due to the melting, the continuation of dechlorination can be evidenced from the increase in the dechlorination efficiency with increase in exposition time at 500 °C. At this temperature and 140 min of exposition time, the % yield is found to reach an asymptote that could also be attributed to the low availability of CuCl. Figure 6 shows an increase in dechlorination efficiency with decrease in the particle size, however the rate of removal was observed to be higher at the elevated temperatures as compare to low temperatures. A decrease in the particle size would increase the rate of decomposition reaction due to the larger surface area facilitating better contact between the reactants. Figure 7 shows the effect of heating duration and particle size of samples on dechlorination efficiency of CuCl residue (roasting temperature is 426.67 °C). Either an increase in the exposition time or a decrease in the particle size increases the decomposition efficiency. The highest dechlorination rate is observed correspond with the longest exposition time and the largest particle size.

Process optimization and the phase changes in the roasting process

The optimum conditions for dechlorination efficiency are obtained by means of the model equation and the optimizer option available with the Design Expert Software. These optimal conditions are identified to be a temperature of 426.67 °C, exposition time 125.33 min and particle size of 0.12 mm. The experiments were repeated at the optimized process conditions to ensure its acceptability. An average value of the repeated experiments at the optimized conditions is 92.79% (Table VI).

The agreement of the model to the experimental results indicates the success of the optimization exercise.

Phase changes in the roasting process

The samples generated under the optimized process conditions were subjected to characterization using X-ray diffraction. Figure 8 shows that the peak of chloride becomes weak distinctly as the main phase has been transformed into CuO, which confirms the transforming of CuCl to CuO.

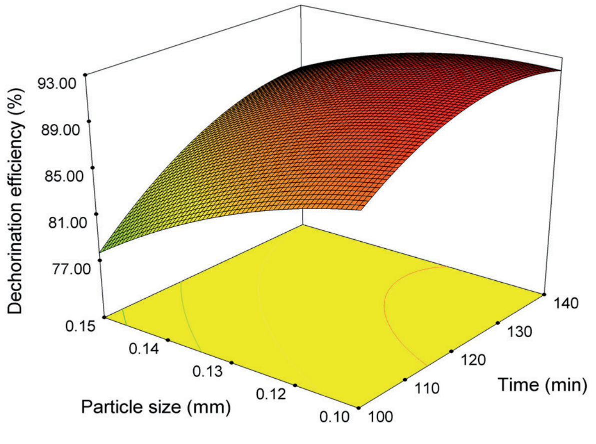


Figure 7. Three-dimensional response surface and contour plot of exposition time vs. particle size on dechlorination efficiency.

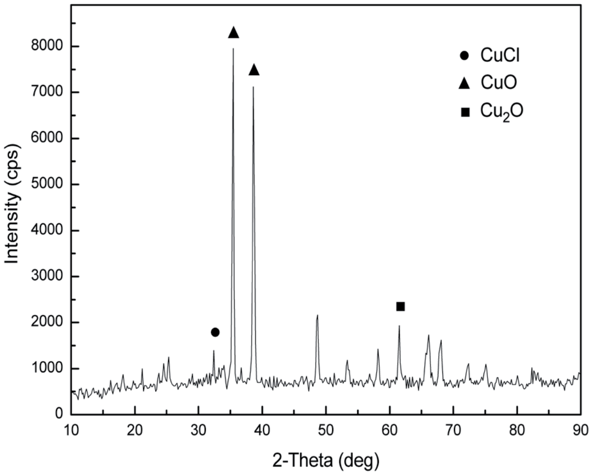


Figure 8. XRD pattern of samples after microwave roasting.

Table VI. Predicted and experimental values of the responses at optimum conditions.

Temperature (°C)	Time (min)	Particle size (mm)	Dechlorination (%)	
			Predicted value	Experimental value
426.67	125.33	0.12	94.23	92.79

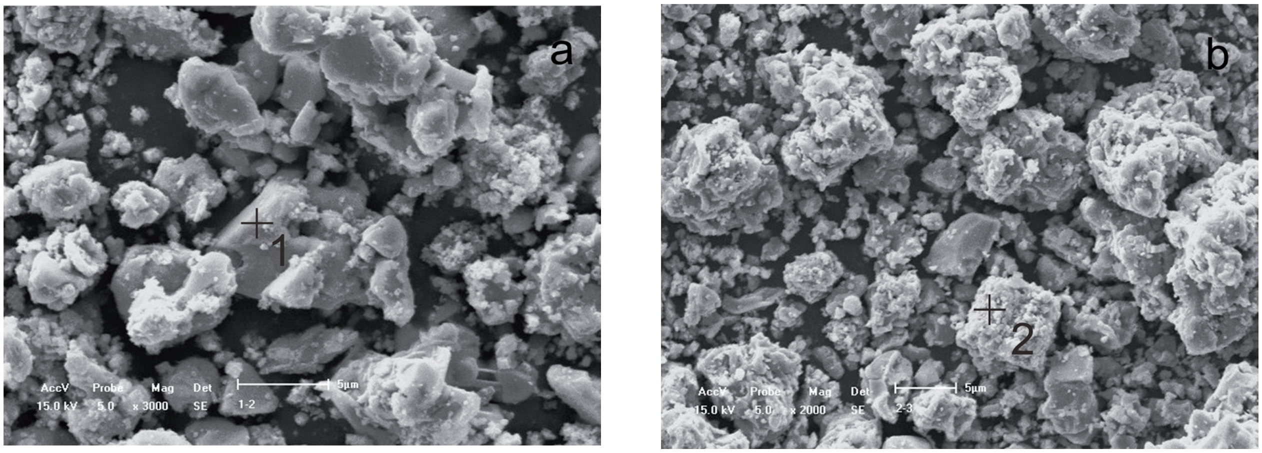
SEM and EDS of residue before and after microwave roasting

The results of the analysis conducted by SEM and EDS are shown in Figure 9 and Table VII.

Table VII. The EDS analysis results of different regions of samples in Figure 9 (atom ratio).

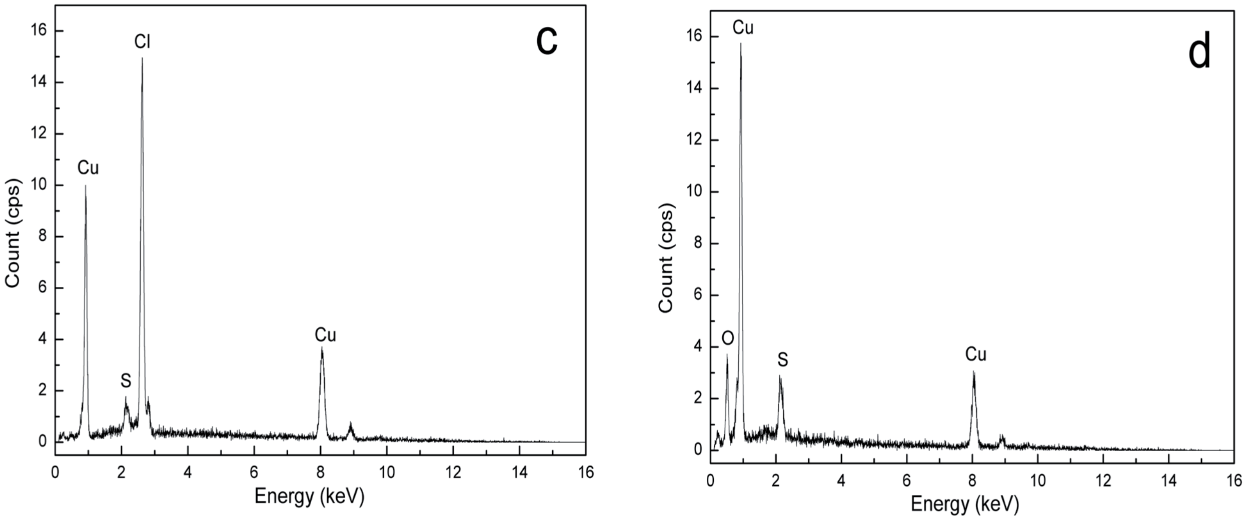
Spot No.	Cu (%)	Cl (%)	O (%)	S (%)
1	52.221	44.855	0	2.924
2	44.149	0	52.502	3.349

It can be seen in Figures 9a and b that the surface of the thermal decomposed residue is distinctly different from the virgin sample. The de-chlorinated sample evidence formation of small crystals on the surface, which could be due to the elimination of Cl from the original CuCl residue and formation of CuO crystals. The EDS patterns shown in Figures 9c and d and the results are in Table II evidence of a high dechlorination efficiency of microwave roasting, which is in accordance with the results given in Table III.



a) Samples before microwave roasting.

b) Samples after microwave roasting.



c) EDS result of spot "1" in (a).

d) EDS result of spot "2" in (b).

Figure 9. SEM and EDS analysis results of samples before and after microwave treatment.

CONCLUSION

Response surface methodology and the central composite design are appropriate for determining the optimal conditions for dechlorination process of the CuCl residue by microwave roasting. The mathematical model is established using sets of experimental data and analysis of variance and the R^2 values of all parameters show a good fit of the model with experimental data. Process optimization is carried out and the optimum conditions for maximizing the dechlorination efficiency are identified to be a roasting temperature of 426 °C, heating duration of 125 min and particle size of samples 0.12 mm. Under optimum conditions, the obtained experimental dechlorination efficiency of 92.79% is found to agree satisfactorily with the predicted value of 94.23%. The comparison of X-ray diffraction patterns shows that most of CuCl in residue has been removed by transforming into CuO and the EDS energy patterns evidence the high dechlorination efficiency of microwave roasting.

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