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Magnesium chloride precipitation from mixed salt solution using 1,4-dioxan: Optimizing the recovery and purity

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ABSTRACT

The precipitation reaction of hexa-aquadichloromagnesium-1,4-dioxan ($MgCl_2 \cdot 6H_2O \cdot C_4H_8O_2$) from saline solution was studied. The influence of eight parameters [temperature, reaction time, stirring speed and mass ratios R1 ($MgCl_2/H_2O$), R2 ($NaCl/H_2O$), R3 (KCl/H_2O), R4 ($MgSO_4/H_2O$) and R5 (dioxan/H_2O)] on selectivity and efficiency of the considered reaction was investigated using the design of experiment methodology. First, the influential factors were determined through a screening approach. Results showed that the compound purity is only sensitive to R2 and R3 mass ratios. Concerning the reaction yield, it depends on mass ratios R1 and R5 and temperature. A model was then established for each response to predict its variation versus the relevant parameters. The obtained models were used to determine the best conditions for hexa-aquadichloromagnesium-1,4-dioxan precipitation from a natural solution. The optimum temperature and mass ratio dioxan/water were 20 °C and 53.25%, respectively. Under these optimal values, the reaction productivity was 42.17% and $MgCl_2 \cdot 6H_2O \cdot C_4H_8O_2$ purity was over 99%. The design of experiment methodology is then suitable for studying processes with several input factors by performing just few experiments.

1. Introduction

Magnesium chloride has several properties that make it useful for various industrial and agricultural applications. In nature, this salt is usually present with other compounds such as NaCl, KCl and $MgSO_4$. Therefore, the raw material often requires treatment to recover it in solid form (Büchel et al., 2000).

One of the treatments adopted is based on the use of dioxan to precipitate magnesium chloride as $MgCl_2 \cdot 6H_2O \cdot C_4H_8O_2$ (hexa-aquadichloromagnesium-1,4-dioxan) (Jin et al., 2014). A drying of the obtained precipitate at constant temperature gives a high purity magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) (Aubry and Bichara, 1979; Fezei et al., 2011). The promising results, obtained with this approach, prompted us to extend investigations on the use of dioxan and study the influence of some parameters on the performance of the corresponding precipitation reaction and its selectivity.

When studying processes having different input factors, the usual experimental approach consists in varying one factor at a time while keeping the others constant, thus enabling to measure the influence of each factor separately. However, this approach ignores any interaction between factors, and therefore leads to wrong conclusions. Design of experiment methodology, on the other hand, seems to be more suitable for this kind of studies. Indeed, it has the dual advantage of taking into account combined effects of several input factors and requiring only a moderate number of experiments (Goupy, 1999).

In the present work, the second strategy was adopted for the first time to study the precipitation reaction of $MgCl_2 \cdot 6H_2O \cdot C_4H_8O_2$ from salty solutions. The objective is twofold. First, it aims at highlighting the factors influencing the purity and recovery of the precipitate. The second purpose of this study is the establishment of a mathematical model expressing the relationship of each response with the influential parameters. The developed models will be used to optimize the $MgCl_2$ recovery from a natural brine.

2. Experimental

2.1. Materials

Five commercial reagents were used to implement this work. The studied salty solutions were prepared using magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$, Labochimie, 98%), sodium chloride (NaCl, Chemi-pharma, 99%), potassium chloride (KCl, Chemi-pharma, 99%) and magnesium sulfate heptahydrate ($MgSO_4 \cdot 7H_2O$, Chemi-pharma, 99.9%). Treatment of these solutions was carried out by the addition of pure 1,4-dioxan ($C_4H_8O_2$, Fluka).

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2.2. Experimentation and analyses methods

All experiments were performed in a jacketed glass reactor under mechanical stirring and constant temperature. For each run, the resulting precipitate was recovered by filtration and characterized by X-ray diffraction (PHILIPS PW 1730/10). Moreover, sulfate, magnesium and alkaline ions concentrations were determined using gravimetry, EDTA complexometry and Flame Atomic Absorption Spectroscopy (FAAS), respectively. The obtained values were used to calculate the experimental responses.

2.3. Calculation

Experimental designs elaboration and data treatment were performed using the NEMROD software (Mathieu and Phan Tan Luu, 1999).

3. Results and discussion

3.1. Screening of factors

The purpose is the determination of the factors affecting the precipitation reaction yield and its selectivity. Eight quantitative parameters were investigated and a Plackett–Burman factorial design was applied. This type of screening design is often used when there are relatively many factors under consideration. It allows knowing the main effects of a great number of parameters with relatively few experiments (Goupy, 2005). In our case, only twelve experiments were run to determine how the eight factors influence the reaction yield (Y_1) and the precipitate purity (Y_2).

The effect of each parameter was evaluated by varying it between the levels given in Table 1. These levels are chosen according to the reagent properties, data of preliminary experiments and equipment abilities.

Table 2 shows the Plackett–Burman design and the experimental responses Yi. According to the results obtained (Table 2), the effects (bi) of the investigated factors were calculated using the NEMROD software and tested for significance by the Student's t-test at 95% confidence level (Mathieu and Phan Tan Luu, 1999).

Fig. 1 shows the graphical representation of these effects (Ghariani and Fezei, 2015). It can be seen that the reaction selectivity is only influenced by the mass ratios R2 ($NaCl/H_2O$) and R3 (KCl/H_2O). These two parameters have a negative effect on the precipitate purity. Therefore, the increase of both mass ratios decreases the product purity. This is probably due to a rise of impurities concentration.

Concerning the reaction yield, the influential factors are in order of importance the mass ratio R1 ($MgCl_2/H_2O$), the temperature and finally the mass ratio R5 (dioxan/H_2O). The effect of temperature on the reaction efficiency is negative, while that of mass ratios R1 and R5 are positive. Consequently, the decrease of temperature and increase of ratios R1 and R5 lead to improve the reaction efficiency. The favorable effect of lowering temperature on $MgCl_2$ recovery yield is most likely due to the exothermic character of the considered precipitation reaction and the expansion of $MgCl_2 \cdot 6H_2O \cdot C_4H_8O_2$ area in the ternary phase diagram $MgCl_2$-dioxan-water. Concerning R1 and R5 mass ratios, the yield improvement can be explained by the displacement of the mixture-point geometric position (in the ternary phase diagram $MgCl_2$-dioxan-water) towards that of $MgCl_2 \cdot 6H_2O \cdot C_4H_8O_2$, which favors its precipitation (Jin et al., 2014; Aubry and Bichara, 1979).

For the other factors, they have a negligible effect on the precipitate recovery and its purity.

Besides the graphical study, the significance of the estimated effects was also assessed from a Normal probability plot (Fig. 2), where the significant effects are those deviating from the normal probability line (Montgomery, 2005).

Thus, the first goal of the study was achieved. Among the eight studied parameters, selectivity

of the precipitation reaction depends only on mass ratios R2 ($NaCl/H_2O$) and R3 (KCl/H_2O). However, the factors affecting the reaction yield are the mass ratios R1 ($MgCl_2/H_2O$), R5 (dioxan/H_2O) and temperature.

Table 1
Studied factors and experimental field.

Coded variable	Natural variable	Factor	Unit	Levels −1	Levels +1
X_1	U_1	Mass ratio $MgCl_2/H_2O$ (R1)	%	37	43
X_2	U_2	Mass ratio $NaCl/H_2O$ (R2)	%	0	1.2
X_3	U_3	Mass ratio KCl/H_2O (R3)	%	0	1.8
X_4	U_4	Mass ratio $MgSO_4/H_2O$ (R4)	%	0	1.2
X_5	U_5	Mass ratio dioxan/H_2O (R5)	%	20	70
X_6	U_6	Working temperature (T)	°C	20	40
X_7	U_7	Reaction time (Rt)	min	30	60
X_8	U_8	Stirring speed (Ss)	rpm	400	800

Table 2
Plackett–Burman design and measured responses.

Run	Factors (natural variables)								Responses (%)	
	U_1	U_2	U_3	U_4	U_5	U_6	U_7	U_8	Y_1 (yield)	Y_2 (purity)
1	43	1.2	0.0	1.2	70	40	30	400	45.69	99.84
2	37	1.2	1.8	0.0	70	40	60	400	16.21	99.81
3	43	0.0	1.8	1.2	20	40	60	800	25.14	99.87
4	37	1.2	0.0	1.2	70	20	60	800	25.91	99.78
5	37	0.0	1.8	0.0	70	40	30	800	9.38	99.90
6	37	0.0	0.0	1.2	20	40	60	400	10.11	100.0
7	43	0.0	0.0	0.0	70	20	60	800	43.72	100.0
8	43	1.2	0.0	0.0	20	40	30	800	27.14	99.82
9	43	1.2	1.8	0.0	20	20	60	400	41.04	99.59
10	37	1.2	1.8	1.2	20	20	30	800	23.18	99.60
11	43	0.0	1.8	1.2	70	20	30	400	49.53	99.76
12	37	0.0	0.0	0.0	20	20	30	400	17.24	100.0

3.2. Modeling

This part is dedicated to the development of a mathematical model expressing the relationship of each response with the relevant parameters. The purity will first be treated followed by the reaction productivity.

3.2.1. Reaction selectivity

Since the purity values are very high and vary slightly in the considered experimental field, it is unreasonable to consider a new experiment to model this response. We simply used the Plackett–Burman design results (Table 2) to develop a predictive model able to explain the influence of the mass ratios R2 ($NaCl/H_2O$) and R3 (KCl/H_2O) on precipitate purity. Therefore, the screening design performed in the first part of the study becomes a 2^2 full factorial design replicated three times. This design (Table 3) was used to fit a linear polynomial model with first order interaction terms (Eq. (2)):

$$Y_2 = b_0 + b_2X_2 + b_3X_3 + b_{23}X_2X_3 \quad (2)$$

where Y_2 is the purity, b_0 the average value of the experimental responses, b_2 and b_3 are the main effects of the factors R2 and R3, b_{23} the effect of interaction between the factors R2 and R3.

Coefficients of the postulated model were calculated by the least squares method and tested for significance by the Student's t-test (Ghariani and Fezei, 2015; Montgomery, 2005). The details are given in Table 4. By eliminating the coefficients which are not significant at 95% confidence level, the regression equation (Eq. (2)) becomes:

$$Y_2(\text{Purity}) = 9.83 - 0.091X_2 - 0.076X_3. \quad (3)$$