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Modeling and Optimization of Struvite Crystal Scaling Using Experimental Design Methodology For Maleic Acid

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***Abstract*— This paper presents results of an investigation of scaling of magnesium ammonium phosphate hexahydrate (struvite) on a process batch crystallizer. In this study, variables, namely temperature (30-40°C), stirring speed (200-400 rpm), maleic acid concentration (1-20 ppm) were optimized using RSM (response surface methodology) to provide the optimum yield of the mass scales. The RSM prediction provided that the maleic acid concentration was the most significant factor for scale yield, while the temperature and the stirring speed were insignificant factors determining the optimal condition of the mass scale yields. The optimum mass scale response of 10.43 mg was obtained at a temperature of 30 °C, stirring speed of 300 rpm and maleic acid concentration of 20 ppm, respectively. This gave the best combination of process parameters for struvite crystallization in an aqueous solution.**

Keywords*— *Response surface methodology (RSM), Struvite crystallization, XRPD Rietveld analysis

I. INTRODUCTION

Struvite is a common mineral deposit found in pipes, pumps and other industrial equipment [1,2]. Precipitation of struvites may interfere with equipment performance and lead to increased maintenance costs. However, struvite precipitation is now considered a prospective technology for phosphate recovery from wastewater treatment, municipal waste, industrial waste and liquid fertilizer [3,4]. Lately the seclusion of struvite is attractive [4], because the final product has a potential market for the fertilizer industry. This can be achieved only by controlling the properties of the crystalline product, reflecting the composition of nitrogen (N), phosphor (P) and magnesium (Mg) ions in the same molar concentration [5]. While the purity and size of the crystal product can be obtained from the precipitation process by controlling the parameters and in designing the equipment [6]. Indeed for struvite precipitation, the nature and quantity of the final product in shape has been of considerable concern to all crystal products in order to be economically viable. As a result, the purity and size of the crystals have been handled for reuse as fertilizer, while the granules formed must be strong enough. Purity is sometimes in control for environmental reasons. An economic return of this crystallization process has been previously reported for the struvite production in the wastewater. [7]. Phosphorus (P) is one of the main chemical elements on earth but does not exist in the form of simple compounds. This is combined with other elements (oxygen, hydrogen) to form phosphates. Although phosphorus (P) is essential for all living organisms, it is closely related to eutrophication. The eutrophication phenomenon comprises surface water nutrient enrichment, which causes an increase in excessive vegetation such as algae, which alters green water in reservoirs, rivers, coastal waters and the marine environment in general [8].

Phosphate is the main source of P commonly used as fertilizer, detergent or insecticide. Traditional P collection processes with phosphorus fixation on mud activation either with biological approach (biological nutrient removal) or chemical (metal salt deposition). This process is efficient in the sense that they can reduce P concentration in liquid waste to approximately 1 mg / L [5], but causes nutrient accumulation (P, N) in the sludge and contributes to the reaction of magnesium and ammonium ions resulting in struvite deposits as a crystalline crust affecting the efficiency of the treatment process, including dilution of struvite crystals in waste water [9] , preventive measures with iron salt [10] or addition of chemical inhibitors [4,6]. To reduce the struvite deposits as crystalline crusts generally use inorganic additives [11,12], [13] or organic additives [14],[15].

There are several key requirements that are effective as additives are: 1. Available easily. 2. Effective at low concentrations. 3. Cheap and significantly will not affect the cost of production. 4. Ideal and non-toxic to the environment.

5. Reduce mineral formation or prevent nucleation. Carboxylic acids as additives meet many of the above requirements [15]. However, many studies to date have not focused on the characteristics of similarities and differences. Efforts to understand the long-term process of mineral stability involved in complex, homogeneous, chemical equilibrium systems require qualitative and quantitative qualitative mineralization of the precipitate. In addition, quantitative mineralogical characterization is required for efficient quality control in a variety of crystalline morphology and struvite purity. These results also provide important insights for crystal growth on natural conditions and within the laboratory. Therefore, this study is needed to better understand how maleic acid as an additive can affect the nucleation and growth of struvite crystals and observe the impact on the quality of struvite products as a fertilizer.

The present study was undertaken of an investigation of scaling of magnesium ammonium phosphate hexahydrate (struvite) on a process batch crystallizer. The variables investigated were temperature, stirring speed, maleic acid concentration were optimized using RSM (response surface methodology) to provide the optimum yield of the mass scales.The crystalline solid product was then characterized using XRPD method the mineral composition.

II. MATERIALS AND METHODS

A. *Preparation of Crystal-Forming Solution*

The supersaturated solutions for the experiments were prepared mainly containing $MgCl_2.6H_2O$ and $NH_4H_2PO_4$ with analytical grade chemicals (Merck™), without further purification. In this way, both powder crystals were separately dissolved in a double distilled water to provide the equimolar of 0.30 M for each ion Mg^{2+}, NH^{4+} and PO_4^{3-}. The pH of both solutions was adjusted to 9 by adding 0.5 N KOH solution. The effect of temperature (30°C, 35°C, 40°C), stirring speed (200, 300, 400 rpm), maleic acid concentration (1,10,20 ppm) Was evaluated in this work. In this case, crystals citric acid were dilute and added into $MgCl_2$ solution. The precipitation process was monitored by reducing the pH solution [11]. The mass of dried precipitate was weighed using Sartorius weigh scale.

B. *Materials Characterization*

Scanning electron microscopy (SEM) (JEOL JSM 5200) and energy dispersive X-ray spectroscopy (EDX) were used to examine the precipitate crystals struvite. In this way, the dried precipitates with different particle sizes below 300 μm were previously embedded in epoxy on an Al-sample holder and sputtered with carbon for SEM/EDX analysis.

Phase identification of the precipitate was conducted by X-ray powder diffraction (XRPD) (Philips 1830/40) measurement. The scan parameters (5-85° 2θ, 0.020 steps, 15 s/step) were set-up for recording XRPD data of the sample. A PC-based search- match program (Philips X'Pert Plus) was initially employed for identifying candidate crystalline phases, which was subsequently verified by the Rietveld method available in the program [16]. The obtained values of the cell parameters and the calculated (wt. %) levels of mineralogical phases were calculated by the program.

C. *Experimental Design and Optimization of Parameters*

In this present study, the input variables temperature, stirring speed, maleic acid concentration and the yield response of the optimum mass (mg) was performed by SRM given in Table 1. A multiple regression data analysis was conducted by the statistical v.6 software packages (StatSoft, Tulsa, OK, USA). Using this method, the proper response value and mathematical model fitted to the measured data was acquired from the experiments, and the independent variables of optimal conditions.

TABLE I. RANGE AND LEVEL OF INDEPENDENT VARIABLES

Independent variables	*Low Level (-1)*	*Range and Level Center Level (0)*	*High Level (+1)*
Temperature (°C)	30	35	40
Stirring speed (rpm)	200	300	400
Maleic acid Concentration (ppm)	1	10	20

III. RESULT AND DISCUSSION

A. *Properties of Solid Precipitated Crystals*

The corresponding solids were then subjected to XRPD Rietveld method. The crystals are primarily composed of struvite. Upon the quantitative Rietveld analyses, struvite was precipitated in the wastewater streams as the major mineral. Shows the SEM image of the crystals obtained exhibiting aggregate formations of irregular prismatic-like crystalline of struvite. This formation was also confirmed again by EDX analyses, showing the chemical elements of Mg, O, and P corresponds to struvite composition.

B. *Predicted Model and Statistical Analysis*

Model of response variables was optimized using SRM with the input data (Table 1), which consisted of 3 factorial design 2^{3} providing nc = 8, ns = 6, no = 2 and run = 16. Accordingly the concentration range of temperature (X_1 30-40 °C), Stirring speed (X_2 200-400 rpm) and maleic acid Concentration (X_3 1-20 ppm) was selected for the calculation. Factors and their levels for SRM consisted of low level (-1) = 30,200,1 high level (+1) = 40,400,20, and the center point (0) = 35,300,10. The whole design of yield response of mass precipitate (mg) is presented in Table 2.

Based on multiple regression analysis of the experimental data, the optimization resulted in the following second-order polynomial equation in term of code values:

$$\begin{aligned} Y = 30.95597 &- 1.17972 X1 + 0.00652 X12 - 3.1216 X2 \\ &- 0.00213 X22 - 0.04791 X3 + 0.00096 X32 \\ &+ 0.00007 X1X2 + 0.00036 X1X3 \\ &- 0.00013 X2X3 \end{aligned} \qquad (1)$$

Where Y is the yield of mass scale (mg), and X_1, X_2 and X_3 are the coded variables for temperature, maleic acid concentration and stirring speed, respectively. Analysis of variance (ANOVA) was performed for determining significance of the model given in Table 3. The function of more significant variables obviously fits with the quadratic polynomial model of mass scale yield. The influence of the significance of a factor can be seen from F-value and p-value. The quadratic regression model showed the value of determination coefficient (R^2) of 0.964 with no significant lack of fit at p>0.05 which means that the calculated model fitted 95 % of the result and only 3.5 % of the total variation did not fit to the model. The significance of the model was also judget by *F*-test, where *F*-value is defined as the ratio between MSF (mean squares of factor) of the MSE (mean squares of error). A factor can be said to have a significant effect when the *F*-value is greater than *F*-table.

TABLE II. DESIGN OF EXPERIMENTS WITH INDEPENDENT VARIABLES

Source	*Sum of squares (SS)*	*Degree of freedom (DF)*	*Mean Square (MS)*	*F-value*	*F-table*	*R^2*
S.S. Regression	17.323	9	17.323	96.268	4.1	0.964
S.S. Error	1.091	6	0.182			
S.S. Total	18.414	15				

TABLE III. ANOVA ANALYSES OF THE YIELD RESPONSE OF CRYSTALLINE MASS.

Run	*Temperature (°C)*	*Independent variables Maleic acid Concentration (ppm)*	*Stirring speed (rpm)*	*Response mass scale (mg)*
1	30.00	1.00	200.00	12.35
2	30.00	1.00	400.00	13.44
3	30.00	20.00	200.00	11.32
4	30.00	20.00	400.00	11.13
5	40.00	1.00	200.00	12.97
6	40.00	1.00	400.00	14.00
7	40.00	20.00	200.00	11.35
8	40.00	20.00	400.00	12.46
9	26.59	10.50	300.00	11.05
10	43.41	10.50	300.00	13.73
11	35.00	-5.98	300.00	13.59
12	35.00	25.98	300.00	10.96
13	35.00	10.50	131.82	12.97
14	35.00	10.50	468.18	13.73
15	35.00	10.50	300.00	11.42
16	35.00	10.50	300.00	11.42

The experimental results were analyzed in chart Pareto (Figure 1). Upon the analysis, p-value less than 0.05 is considered to have an insignificant effect contributed to the response. On the basis of the results given in Figure 1, it can be seen that maleic acid Concentration (X2) has major linear (L) effect for controlling struvite production, followed by Temperature (L) (X1) and stirring speed (X3); and their quadratic effects (Q) for stirring speed (X3)2, Temperature (X1)2 and maleic acid Concentration (X2)2. However, the quadratic effect of maleic acid Concentration (X2)2 can be ignored because they provide insignificance on the yield response of the mass scales.

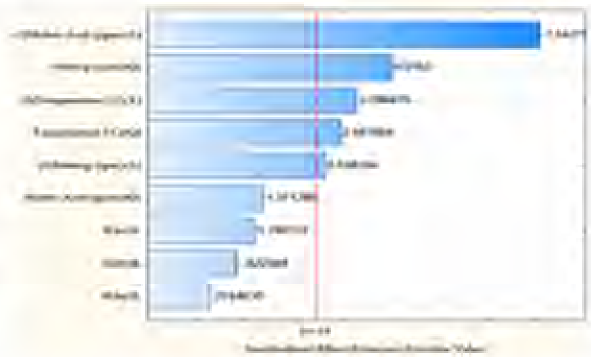

Fig. 1. Pareto Chart of Optimization Independent Variables on The Yield Response of Struvite Production. (L) Is The Linear and (Q) Is The Quadratic Interaction of Variables.

C. *Optimization of Independence Variables for the Optimum Struvite Production*

The graphical results of interactive independent and dependent variables are depicted by 3D and 2D contour plots, which enable to determine the optimum recovery of struvite (mass in mg) (Figs. 2-4). Different forms of the contour plots indicate the different interactive effects, where the significant interactions between the variables is shown in an elliptical contour plot. In contrast, a circular contour plot shows the insignificant interactive effects.

Figure 2 presents the interaction between temperature and maleic acid concentration for the yield of struvite. As expected, the yield of struvite increases when the highest temperature is applied. However, the presence of increased maleic acid concentration led to the reduced production of struvite.

Figure 3 presents the interaction between maleic acid concentration and stirring speed and the yield of struvite. When the stirring speed increase the high amount of struvite could be produced, while the increasing maleic acid concentration show the reduced production of struvite. Both temperature and stirring speed have significant effects on the struvite production.

Figure 4 presents the interaction between temperature and stirring speed on the yield of mass scale. Apparently, the increase of temperature from 30 to 35 °C makes a decrease in the struvite production. Similarly, the increase of stirring speed from 200 to 300 °C in the decrease of struvite production.

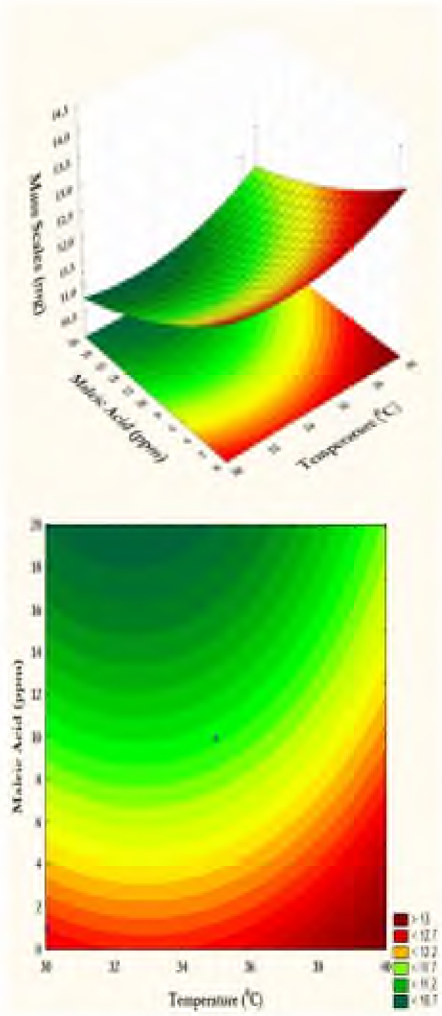

Fig. 2. Response Surface Contour for Mass Crystal Production Between Temperature and Maleic Acid Concentration.

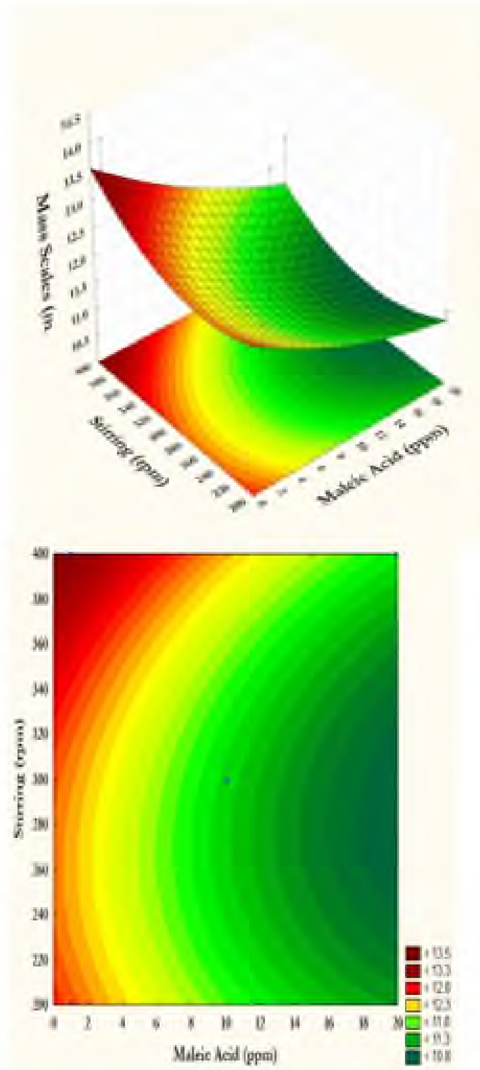

Fig. 3. Response Surface and Contour Plot for Interaction on Mass Crystal Production Between Maleic Acid Concentration and Stirring Speed.

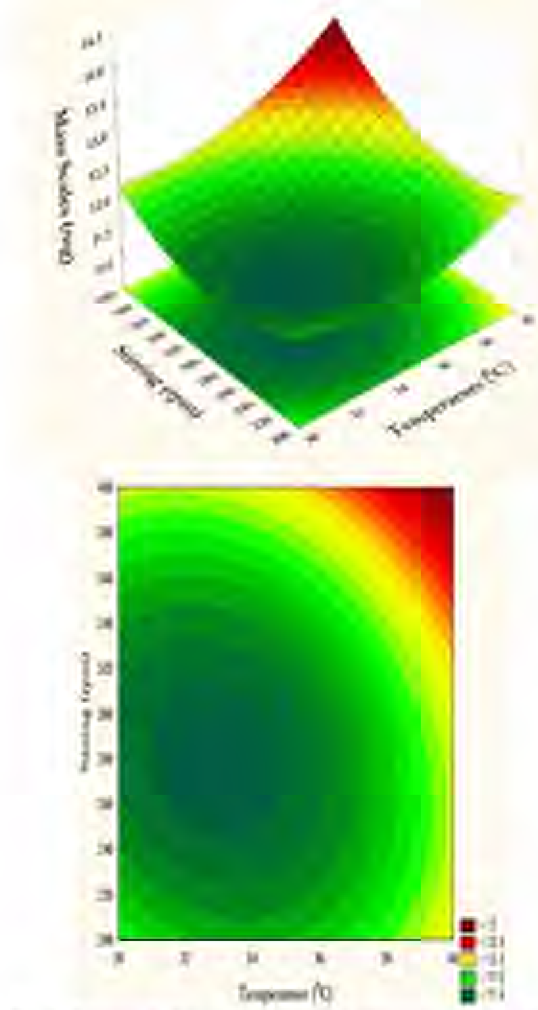

Fig. 8. Response Surface and Contour Plot for Interaction on Mass Crystal Production Between Temperature and Stirring Speed.

Further, the optimum mass scales was obtained by entering values into the equation, which include the optimum ratio of the mass response for variable optimization. Optimum mass scales are presented in Table 4.

TABLE IV. OPTIMUM MASS SCALES (MG)

Factor	*Optimum State*	*Optimum Mass Scales (mg)*
Temperature (°C)	32.07	
Maleic acid concentration (ppm)	19.68	10.432
Stirring speed (rpm)	306.54	

D. Validation of the Predicted Value for the Optimal Variables.

The optimum values of the process variables were then verified using the experimental data. The optimum yield of struvite was calculated using the each temperature (32.07 ppm), maleic acid Concentration (19.68 ppm) and stirring speed (306.54 rpm) and resulted in 10.432 mg of the precipitated struvite [Table 4]. Additionally, the experimental result of the mass scale at these concentrations was 10.825 mg [Table 5]. Here the calculated % error for for the mass scale response was 3.75%. This means for the estimated response of struvite production has an accuracy of 96.25%.

TABLE V. OPTIMUM CONDITIONS AND THE PREDICTED AND EXPERIMENTAL VALUE OF RESPONSE AT THE OPTIMUM CONDITIONS

Optimum variables		*Optimum Result*	*Experimental Result*	*% Relative error*
			Mass Scales	
Temperature (°C)	32.07			
Maleic Acid Concentration (ppm)	19.68	10.432	10.825	3.759
Stirring Speed (rpm)	306.54			

* [illegible]

IV. CONCLUSIONS

SRM optimization of variable concentrations of heavy metals in the wastewater provided that the availability of Maleic acid concentration has a significant effect on the mass yield of struvite during precipitation. The optimum result of the mass response scale (10.432 mg) was related to temperature (30 ppm), maleic acid Concentration (20 ppm) and stirring speed (300 rpm) respectively. Accordingly, a good achievement of modeling and optimization of struvite precipitation was presented in this paper. The influence of selected parameters and thus model validation with insignificance parameters could be confirmed. Finally, an easy, simple, and cost effective method for wastewater treatment and precipitation of a valuable fertilizer product rich in phosphorous would likely to be implemented.

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