U.P.B. Sci. Bull., Series B, Vol. 73, Iss. 2, 2011 ISSN 1454-2331

OPTIMIZATION OF COAGULATION-FLOCCULATION PROCESS WITH ALUMINUM SULFATE BASED ON RESPONSE SURFACE METHODOLOGY

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În această lucrare a fost studiat procesul de coagulare – floculare pe bază de sulfat de aluminu, pe baza metodologiei suprafețelor de răspuns (RSM), pentru stabilirea parametrilor optimi în vederea atingerii unui grad maxim de limpezire:doza de aluminiu, turbiditatea inițială şi pH-ul apei. Metodologia suprafețelor de răspuns reprezintă un instrument util, care, pe baza experienței acumulate de un operator, permite determinarea rapidă, printr-un număr mic de determinări, a condițiilor optime de lucru, pentru atingerea unui grad de limpezire maxim.

A coagulation-flocculation process, based on aluminum sulfate, has been studied by using Response Surface Methodology (RSM), in order to establish the optimum parameters to achieve a maximum suspensions removal: Al dosage, initial turbidity and water pH. RSM is an useful tool, which allows a treatment plant operator, based on his or her experience, to determine easily, after a small number of trials, the optimum conditions to achieve a maximum suspensions removal efficiency.

Keywords: coagulation-flocculation, water treatment, analysis of variances, Response Surface Methodology, aluminum sulfate

1. Introduction

For a very long time, aluminum sulfate is a well known coagulant, being used in water and wastewater treatment as a preferred reagent. Usage of aluminum sulfate is based on several advantages, as low cost, high efficiency at low doses, low toxicity and high availability [1]. As it is well known, the coagulation-flocculation purpose is to remove colloidal suspensions, both inorganic (clays, silts) or organic (humic compounds), which could be a good support for pathogens development, and presents a great threat to drinking water aspect [2]. Thus, the main purpose is to attain a high removal of colloidal suspensions, while

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obtaining large, heavy, and strong flocs, a lower water loss [3], and a minimum amount of residual Al in treated water [4-7]. All the above mentioned criteria should be used to describe coagulation-flocculation efficiency.

Efficiency and mechanism of coagulation-flocculation process depend on several factors, the most relevant being initial turbidity, pH, reagents (coagulant, adjuvant) dosage and type, system hydrodynamics in coagulation and flocculation stages, temperature, alkalinity [8-10].

The optimum conditions of coagulation-flocculation process have been established by using Response Surface Methodology (RSM). RSM is a technique to design factorial experiments, in order to build mathematical models which allow ones to assess the effects of several factors onto a desired response, and to establish the optimum conditions, while number of experiments is to be reduced [3,11]. In this study, initial turbidity, pH and Al dosage have been considered as factors, and the optimization response has been treated water turbidity.

2. Experimental

Coagulation tests have been performed according to jar-test method, using a standard flocculator *Stuart Scientific SW5*, equipped with two mixing posts. As coagulant, a 5% aluminum sulfate solution (density = 1.0291 $g \cdot cm^{-3}$) has been used. Coagulation tests have been performed in 1 liter cylindrical bakers, at 20 ± 1°C, by using stock suspensions prepared from water and soil, with various doses of aluminum sulfate. Coagulation step was done by fast mixing (150 rpm) for 5 minutes, while flocculation step was done for 10 minutes, at 50 rpm, followed by a settling time of 60 minutes. Samples from supernatant have been taken to determine treated water turbidity.

To prepare suspensions, 10 l of water have been mixed with 500 g of chernozem soil, followed by settling for 24 hours. Resulted supernatant has been used in coagulation tests. Initial turbidity has been adjusted by adding fresh water.

Turbidity has been determined by using Jenway 6405 UV-vis spectrophotometer, at two wavelengths: 420 and 500 nm, by using NTU scale.

Coagulant solution was prepared from $Al_2(SO_4)_3 \cdot 18H_2O$ and deionized water. pH adjustment was performed with 1% H_2SO_4 solution or with 1% $Ca(OH)_2$ suspension. All used reagents were analytically pure.

The investigations have been performed by using duplicate determinations.

3. Mathematical apparatus

According to literature data, Response Surface Methodology (RSM) has been developed in 1950s and has been defined by Myers et al. (1989) as “a collection of tools in design or data analysis that enhance the exploration of a region of design variables in one ore more dimensions” [3].

Building a mathematical model based upon RSM is based on the following assumptions: a dependent variable y (response) varies as a function of several independent variables $x_1 \dots x_n$ (factors). Thus it can be defined a function

$$y = f(x_1 \dots x_n) \tag{1}$$

Due to the fact that the factors are expressed in different units and vary in different ranges, they are coded according to equation (2), in order to assess any variable significance [3, 11, 12]:

$$X_i = \frac{x_i - x_{i,0}}{\delta x_i} \tag{2}$$

where X_i represents the coded value of independent variable “i” ;
x_i – uncoded value of independent variable “i” ;
$x_{i,0}$ – median of the data array x_i;
δx_i – step change

Step change δx_i is defined as follows:

$$\delta x_i = \frac{max(x_i) - min(x_i)}{2} \tag{3}$$

Thus, all coded independent variables vary in the range [-1, 1], and any significant variable can be easily evaluated [13, 14]. Function f in equation (1) can be in linear, quadratic or a higher degree polynomial form [3].

4. Results and discussion

The variation of different parameters: Al dosage (x_1), initial turbidity (x_2), and pH (x_3) is presented in Table 1, and its influence on treated water turbidity, which represents response variable (y) has been investigated.

Table 1

Variables ranges

Parameter	Minimum	Maximum
Al dose, mg/l (x_1)	6.5	16.25
Initial turbidity, NTU (x_2)	27 ± 1	53 ± 1
pH (x_3)	3 ± 0.1	10 ± 0.1

The uncoded values of independent variables are:

$$\begin{aligned} Al &= (6.50,\ 9.75,\ 13.00,\ 16.25) \\ T_{in} &= (27,\ 40,\ 53) \\ pH &= (3.0,\ 6.5,\ 10.0) \end{aligned} \tag{4}$$

Experimental results are presented in Table 2.

Table 2

Variables ranges

T_{in} = 27 NTU			T_{in} = 40 NTU			T_{in} = 53 NTU		
Al, mg/L	pH	T_{fin}, NTU	Al, mg/L	pH	T_{fin}, NTU	Al, mg/L	pH	T_{fin}, NTU
6.50	3	6.8	6.50	3	13.8	6.50	3	17.2
9.75	3	13.6	9.75	3	13.4	9.75	3	12.9
13.00	3	15.8	13.00	3	12.7	13.00	3	11.8
16.25	3	14.7	16.25	3	12.6	16.25	3	12.8
6.50	6.5	5.6	6.50	6.5	3.6	6.50	6.5	10.4
9.75	6.5	5.6	9.75	6.5	3.5	9.75	6.5	5.1
13.00	6.5	5.7	13.00	6.5	3.2	13.00	6.5	5.2
16.25	6.5	5.4	16.25	6.5	3.4	16.25	6.5	4.4
6.50	10	6.9	6.50	10	4.2	6.50	10	12.4
9.75	10	8.6	9.75	10	5.7	9.75	10	6.0
13.00	10	9.0	13.00	10	4.7	13.00	10	6.5
16.25	10	7.6	16.25	10	2.3	16.25	10	7.5

Data presented in equation 4 and Table 2, were symbolized as follows:

- Al represents aluminum dose (mg Al/L);
- T_{in} represents initial water turbidity;
- pH – pH value of treated water;
- T_{fin} – final turbidity of treated water.

According to equations (2) – (4), the coded values of independent variables are:

$$\begin{aligned} x_1 &= (-1,\ -1/3,\ 1/3,\ 1) \\ x_2 &= (-1,\ 0,\ 1) \qquad , \\ x_3 &= (-1,\ 0,\ 1) \end{aligned} \tag{5}$$

A quadratic polynomial model has been used to connect the data presented in Table 2, using the coded independent variables according to equation (5) [3, 9-12]:

$$\begin{aligned} y = a_0 + a_1x_1 + a_2x_2 + a_3x_3 + a_4x_1^{\,2} + a_5x_2^{\,2} + a_6x_3^{\,2} + \\ + a_7x_1x_2 + a_8x_1x_3 + a_9x_2x_3 \end{aligned} \tag{6}$$

Parameters in equation (6) have been calculated by linear regression, using a system of 10 equations with 10 unknowns. The equation system has been solved by using software package MathCAD™ 2001 Professional. A weak correlation has been observed after comparing simulated vs. experimental data ($R^2 = 0.8587$). In consequence, a cubic polynomial model has been proposed, according to equation:

$$\begin{aligned} y = {} & a_0 + a_1x_1 + a_2x_2 + a_3x_3 + a_4x_1^2 + a_5x_2^2 + a_6x_3^2 + \\ & + a_7x_1x_2 + a_8x_1x_3 + a_9x_2x_3 + a_{10}x_1^3 + a_{11}x_2^3 + a_{12}x_3^3 + \\ & + a_{13}x_1^2x_2 + a_{14}x_1^2x_3 + a_{15}x_1x_2^2 + a_{16}x_2^2x_3 + a_{17}x_1x_3^2 + \\ & + a_{18}x_2x_3^2 + a_{19}x_1x_2x_3 \end{aligned} \tag{7}$$

Trying to calculate model parameters, according to equation (7), turned to a system of 20 equations with 20 unknowns, which could not be solved due to the fact that its matrix was singular. It is due to the fact that cubic values of coded variables, x_i^3 are identical with values x_i, for $i = 2, 3$. Thus, the model has been simplified, according to equation (8):

$$\begin{aligned} y = {} & a_0 + a_1x_1 + a_2x_2 + a_3x_3 + a_4x_1^2 + a_5x_2^2 + a_6x_3^2 + \\ & + a_7x_1x_2 + a_8x_1x_3 + a_9x_2x_3 + a_{10}x_1^2x_2 + a_{11}x_1^2x_3 + \\ & + a_{12}x_1x_2^2 + a_{13}x_2^2x_3 + a_{14}x_1x_3^2 + a_{15}x_2x_3^2 + a_{16}x_1x_2x_3 \end{aligned} \tag{8}$$

To determine parameters a_0 … a_{16} in equation (8), a system of 17 equations with 17 unknowns had to be solved.

The parameters in equation 8 are presented in Fig. 1. The correlation between experimental output data (treated water turbidity) and the response variable calculated according to equation (8) are presented in Fig. 2.

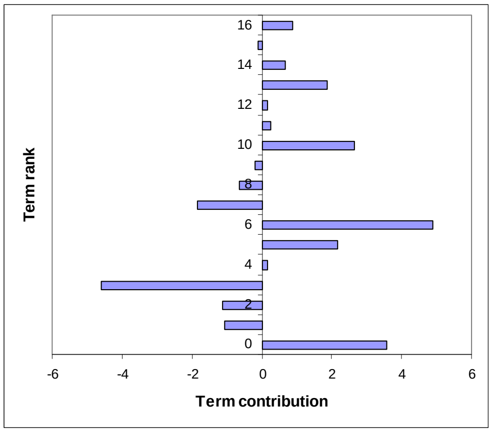


Fig. 1. Contributions of terms in equation (8) on the value of response variable *y*

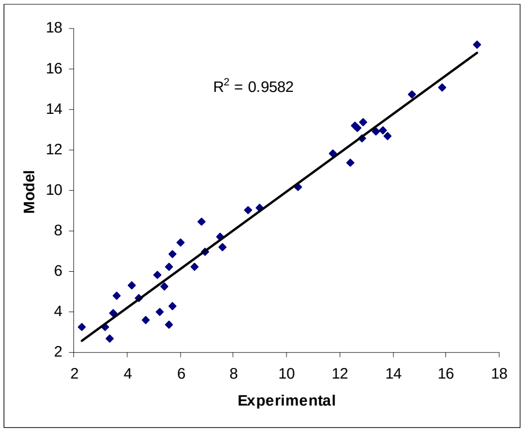
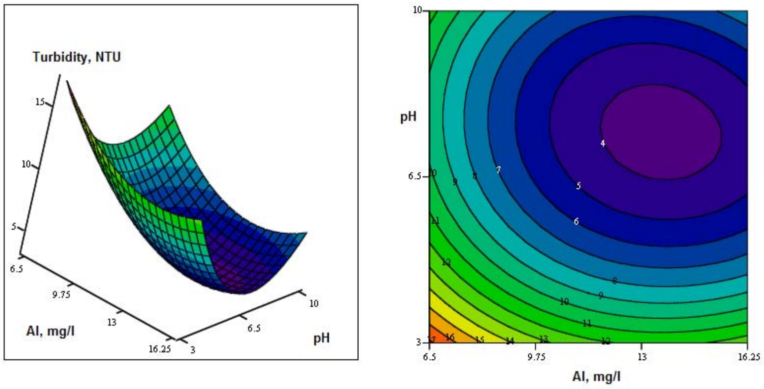


Fig. 2. Scatter plot experimental data (measured turbidity) vs. model output according to equation (8). Straight line indicates a perfect fit.

According to data in Fig. 1, it can be observed that terms x_1^2, x_2x_3, $x_1^2x_3$, $x_1x_2^2$ and $x_2x_3^2$ have a little significance, thus equation (8) can be expressed as follows:

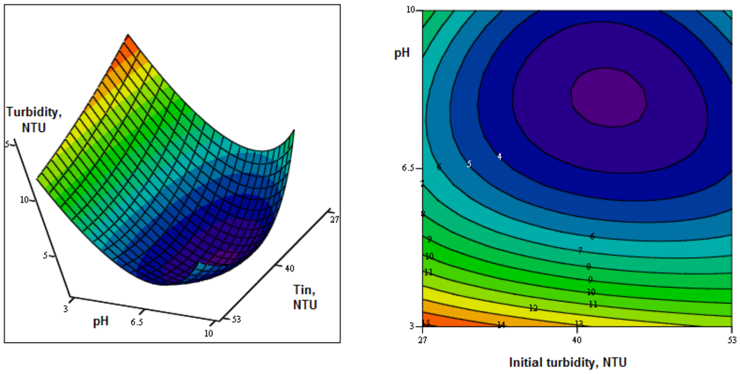
$$y = 3.57 - 1.06x_1 - 1.11x_2 - 4.58x_3 + 2.16{x_2}^2 + 4.88{x_3}^2 - 1.85x_1x_2 - \\ - 0.64x_1x_3 + 2.66{x_1}^2x_2 + 1.87{x_2}^2x_3 + 0.68x_1{x_3}^2 + 0.88x_1x_2x_3 \qquad (9)$$

The graphic representations of parameters influence on final turbidity, based on equation (9), are represented in Figs. 3 – 5.



a b

Fig. 3. Final turbidity as a function of Al dose and pH, at initial water turbidity of 53 NTU.
a – 3D plot; b – contour plot



a b

Fig. 4. Final turbidity as a function of initial turbidity and pH, at Al dose of 14 mg/l.
a – 3D plot; b – contour plot

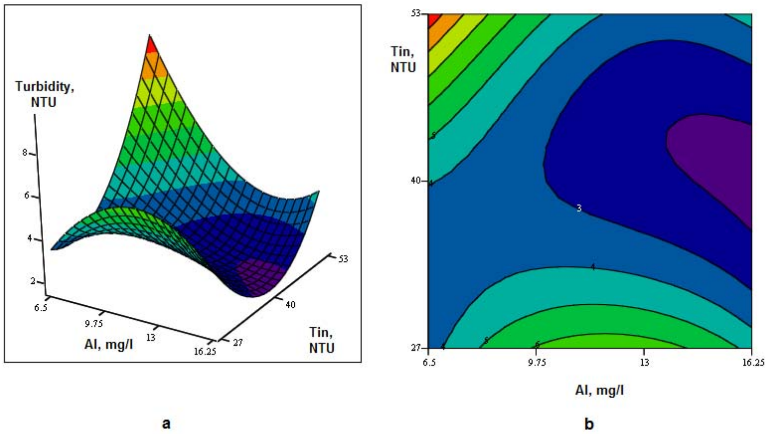


Fig. 5. Final turbidity as a function of Al dose and initial turbidity at pH = 7.5.
a – 3D plot; b – contour plot

Data in Fig. 2 show a square value of correlation coefficient of 0.9582, which indicates a good fit between experimental data and model output. Thus, the proposed model can be successfully used to establish the optimum parameters of coagulation process.

Analyzing the data in Fig. 1, one can observe that all three factors have a significant influence on coagulation efficiency. Thus, an increase of initial turbidity leads o a higher efficiency, while terms $x_2 - x_2^2$ (corresponding to Al dosage), and $x_3 - x_3^2$ (pH) have an opposite significance, indicating an optimum range. This behavior can be easily observed in 3D plots and in their corresponding contour plots, presented in Figs. 3-5.

As shown in Fig. 3, pH and Al dosage have strong effects on suspensions removal efficiency. The optimum domain can be identified at moderate dosages of Al (12 – 15 mg/l) and for pH values corresponding to natural surface waters (6.5 – 8.5).

5. Conclusions

A third order polynomial model has been used to describe the influence of pH, coagulant dose and initial water turbidity on coagulation-flocculation efficiency, based on Response Surface Methodology. This method allowed to establish the optimum parameters for coagulation – flocculation process by using a small number of experiments. A neutral pH, moderate coagulant doses and a higher load in suspensions of raw water presented a favorable influence on suspension removal efficiency.

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