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MODELING OF THE COAGULATION, FLOCCULATION AND PRE-OXIDATION PROCESSING OF THE PRUT RIVER WATER

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Abstract

In this article, it is described the study of the coagulation, flocculation and pre-oxidation processes of the Prut river water, by using reagents such as iron (III) chloride, polyacrylamide and chlorine dioxide. The main goal was to establish the best ratio between the coagulation reagent (iron (III) chloride), flocculation reagent (polyacrylamide) and pre-oxidation reagent (chlorine dioxide), by monitoring the decrease of water turbidity. Through the modeling of coagulation, flocculation and pre-oxidation processes, the turbidity variation was monitored and the best conditions were established in order to obtain minimum values for this parameter that characterizes the quality of drinking water.

Introduction

The water sampled from the river Prut is processed at Chirita Processing Complex using a technology that includes the following stages: capture, coagulation, flocculation, pre-oxidation, pond filtration, disinfection and distribution. The qualities of the processed drinking water that allows it to fall in the category of water suitable for human use are dependent on the quality of the unprocessed water and the performance of each processing stage [1-5]. The physical and chemical characteristics of unprocessed water are shown in Table 1, by mean values. The achievements of various coagulation reagents recommended by various studies, compared by achieved turbidity [6], are presented in Table 2.

Table 1. Physical and chemical analysis of unprocessed water from Prut river

Parameter	Units of measurement	Value
Temperature	°C	22
pH		8.34
Total hardness	°dH	16.39
Temporary hardness	°dH	9.72
Permanent hardness	°dH	6.67
Calcium	°dH	11.92
Manganese	°dH	4.47
Total Al^{+3}	ppm as ion	0.01
NO_3^-	ppm as ion	4.00
NO_2^-	ppm as ion	0.03

Dissolved oxygen	ppm	6.40
Turbidity	^{o}NTU	22.2
Conductivity	$\mu S \cdot cm^{-1}$	419.00
CCOCr	$mg \cdot L^{-1}$	13.8
Constant residue	$mg \cdot L^{-1}$	510
Suspensions	$mg \cdot L^{-1}$	312
CBO_5	$mg \cdot L^{-1}$	1.6

Table 2. The achievements of various coagulation reagents used for processing Prut river water

Parameter	Aluminum sulfate				Aluminum polyhydroxy chloride				Iron (III) chloride			
Unprocessed water	1	2	3	4	1	2	3	4	1	2	3	4
Coagulant reagent concentration ($mg \cdot L^{-1}$)	0.95	1.4	1.9	2.3	0.95	1.4	1.9	2.3	2.5	5	7.5	10
Turbidity (NTU)	20	13.6	11	8.7	14.4	4.5	6.4	8.4	13.5	8.30	6.50	4.10
pH	7.65	7.58	7.45	7.40	7.93	7.82	7.80	7.78	7.66	7.59	7.38	7.30
Residual aluminum concentration in processed water ($mg \cdot L^{-1}$)	0.056	0.083	0.112	0.136	0.061	0.09	0.101	0121	0	0	0	0

The data from Table 2 shows that when aluminum sulfate or aluminum polyhydroxy chloride are used, high concentration of residual aluminum ions is found in processed water, while quality regulations forbid aluminum ions levels higher than 200 ppm. Therefore the use of iron (III) chloride as coagulation reagent was studied, and the results are shown in the Figure 1.

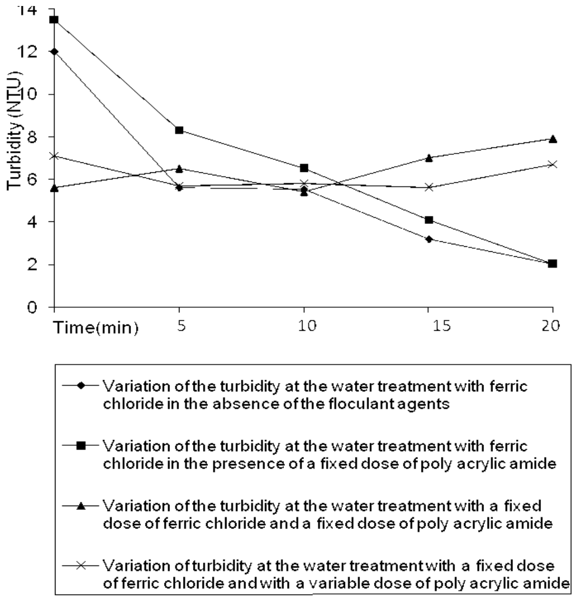


Figure 1. The results obtained when iron (III) chloride was used as coagulant reagent for water processing

Also, it is well known that the used doses of iron (III) chloride show no toxicity for humans, and the concentration of iron ions in processed water is almost undetectable. The analysis of literature data has shown that iron (III) chloride used as coagulant reagent is a modern and toxicity-free solution for water processing. For these reasons, the aim of this study is the modeling of coagulation, flocculation and pre-oxidation processing of Prut water when using iron (III) chloride as coagulant reagent, polyacrylamide as flocculation reagent and chlorine dioxide as pre-oxidant reagent. Also the optimum conditions were established in order to obtain minimum values for the turbidity of drinking water.

Materials and Method

In order to purify the Prut river water by coagulation/flocculation/pre-oxidation the following chemical reagents were used: iron(III) chloride, polyacrylamide and chlorine dioxide and the process evaluation was carried out by turbidity monitoring. The turbidity of unprocessed water was measured using a portable Hach-Lange turbidimeter through the measurement of the transparency of the sample when compared to a formasine standard. Unprocessed water was treated with different amounts of iron (III) chloride, polyacrylamide and chlorine dioxide, and real time turbidity monitoring was performed on-line with a Endress-Hausser laser turbidimeter.

Results and discussions

Based on experimental results and theoretical considerations on the coagulation/flocculation/pre-oxidation processing procedure, the value of turbidity (ye) was chosen as a criterion for optimization modeling. Next, it was established that the independent variables that had a significant influence on turbidity were: the amount of iron (III) chloride used as coagulation reagent (x_1), the amount of polyacrylamide – the flocculation reagent (x_2) and the amount of chlorine dioxide, the pre-oxidant reagent (x_3).

The values of the independent variables and how the variance was applied to value were chosen arbitrarily. Their extreme values and the coding may be found in Table 3.

Table 3. The extreme values and coding of independent variables that influence water turbidity

Factor	Coding	Central and extreme values			Variance value
		Minimum (-1)	Middle (0)	Maximum (+1)	
Amount of coagulation reagent (x_1), iron (III) chloride ($mg \cdot L^{-1}$)	X_1	2.5	7.5	12.5	5
Amount of flocculation reagent (x_2), polyacrylamide ($mg \cdot L^{-1}$)	X_2	0.20	0.35	0.5	0.15
Amount of pre-oxidation reagent (x_3), chlorine dioxide ($mg \cdot L^{-1}$)	X_3	0.10	0.20	0.30	0.1

For mathematical modeling of coagulation/flocculation/pre-oxidation process, a central composed rotatable program was used for three independent variables of second order expanded factorial experiment in the (-a-1), 0, (+1+a) field. There were performed twenty experiments, six of which in the center of the experimental program [7-9]. The experimental matrix and experimental results are presented in Table 4.

Table 4. Experimental matrix and true response

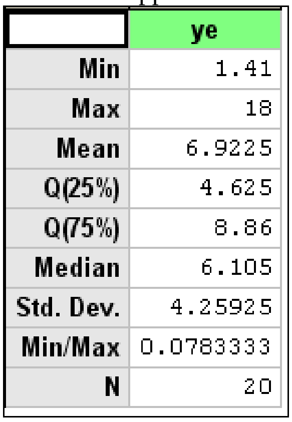
No.	X_1	X_2	X_3	X_1^2	X_2^2	X_3^2	X_1X_2	X_1X_3	X_2X_3	y_{exp}
1	-1	-1	-1	+1	+1	+1	+1	+1	+1	13.5
2	+1	-1	-1	+1	+1	+1	-1	-1	+1	2.35
3	-1	+1	-1	+1	+1	+1	-1	+1	-1	11.85
4	+1	+1	-1	+1	+1	+1	+1	-1	-1	1.96

5	-1	-1	+1	+1	+1	+1	+1	-1	-1	10.61
6	+1	-1	+1	+1	+1	+1	-1	+1	-1	2.08
7	-1	+1	+1	+1	+1	+1	-1	-1	+1	11.92
8	+1	+1	+1	+1	+1	+1	+1	+1	+1	3.88
9	-1.682	0	0	+2.828	0	0	0	0	0	18
10	+1.682	0	0	+2.828	0	0	0	0	0	1.41
11	0	-1.682	0	0	+2.828	0	0	0	0	5.37
12	0	+1.682	0	0	+2.828	0	0	0	0	5.99
13	0	0	-1.682	0	0	+2.828	0	0	0	6.11
14	0	0	+1.682	0	0	+2.828	0	0	0	6.09
15	0	0	0	0	0	0	0	0	0	6.85
16	0	0	0	0	0	0	0	0	0	6.12
17	0	0	0	0	0	0	0	0	0	6.09
18	0	0	0	0	0	0	0	0	0	6.12
19	0	0	0	0	0	0	0	0	0	6.10
20	0	0	0	0	0	0	0	0	0	6.12

The experimental data were processed using specialized MODE[10] software. Parallel determinations (no. 15-20 from Table 4) were used to calculate the experimental error, establishing it to be 3.58%.

The qualitative analysis of the results showed that the makers taken into account significantly influence the decrease of turbidity, because their variation from lower to higher levels lead to a change of turbidity of 16.51 NUT (minimum ye = 1.41 and maximum ye = 18.00). For analysis of the variable characteristics in terms of central tendency, distribution and shape of the scattering, it was called for a MODE application that provided the data in Table 5 for descriptive statistics.

Table 5. Descriptive statistics provided by the MODE application



	ye
Min	1.41
Max	18
Mean	6.9225
Q(25%)	4.625
Q(75%)	8.86
Median	6.105
Std. Dev.	4.25925
Min/Max	0.0783333
N	20

Table 5 showed that the average and the median had similar values allowing us to conclude that the distribution of experimental values was very good. This was confirmed by the histogram shown in Figure 2, which proved that the experimental results were concentrated around the average, indicating small variations, making it possible to control the process.

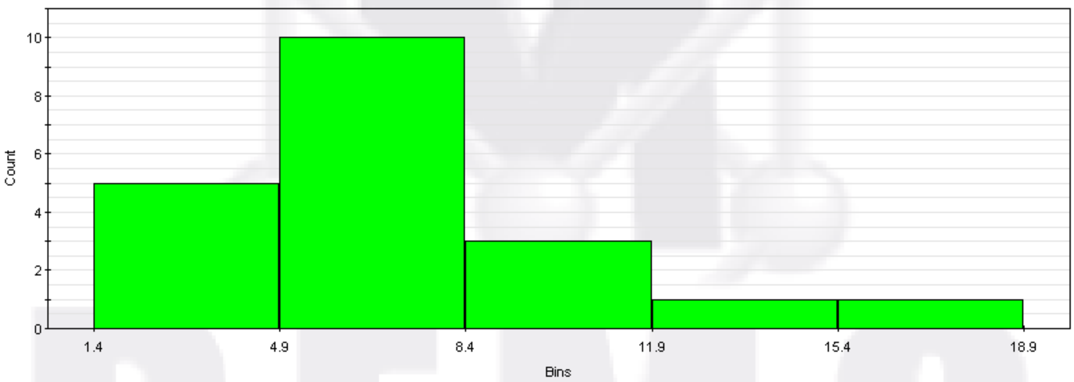
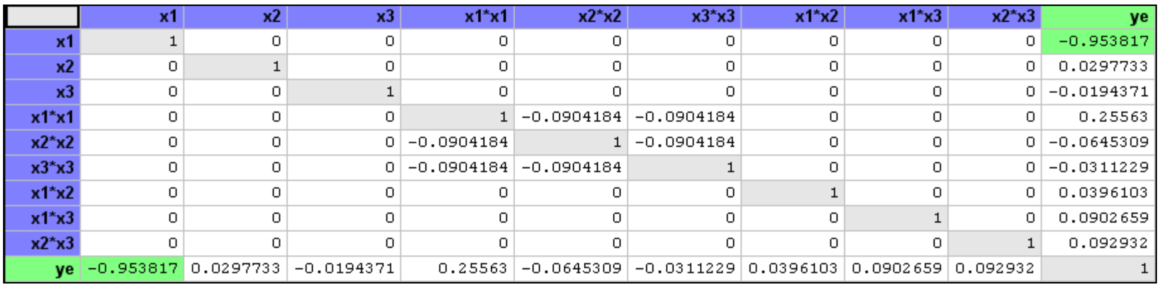


Figure 2. Small dispersion histogram

Also, the MODE application emphasizes the intensity of links between all pairs of variables through the correlation matrix presented in Table 6 and by plotting the linear correlation between response factors, shown in Figure 3.

Table 6. Correlation matrix



	x1	x2	x3	x1*x1	x2*x2	x3*x3	x1*x2	x1*x3	x2*x3	ye
x1	1	0	0	0	0	0	0	0	0	-0.953817
x2	0	1	0	0	0	0	0	0	0	0.0297733
x3	0	0	1	0	0	0	0	0	0	-0.0194371
x1*x1	0	0	0	1	-0.0904184	-0.0904184	0	0	0	0.25563
x2*x2	0	0	0	-0.0904184	1	-0.0904184	0	0	0	-0.0645309
x3*x3	0	0	0	-0.0904184	-0.0904184	1	0	0	0	-0.0311229
x1*x2	0	0	0	0	0	0	1	0	0	0.0396103
x1*x3	0	0	0	0	0	0	0	1	0	0.0902659
x2*x3	0	0	0	0	0	0	0	0	1	0.092932
ye	-0.953817	0.0297733	-0.0194371	0.25563	-0.0645309	-0.0311229	0.0396103	0.0902659	0.092932	1

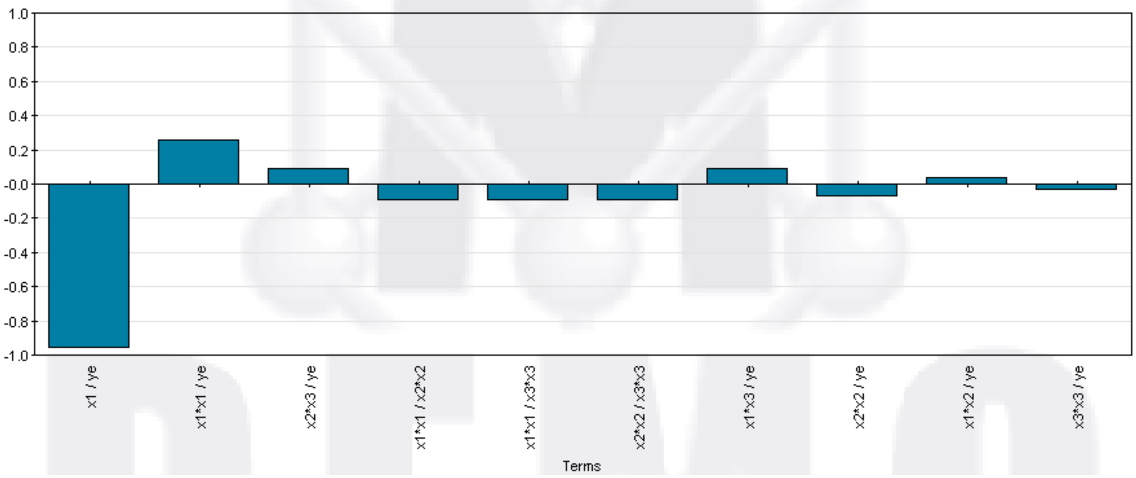


Figure 3. Graphical representation of linear correlation between factors and response

Based on the results provided by the MODE application, the dependence of y_e to x_1, x_2, x_3 variables was best described by the following regression equation:

$$ye = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{11}x_1^2 + b_{22}x_2^2 + b_{33}x_3^2 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3$$

Calculation of regression coefficients was performed by multiple linear regression (MLR). The results of MLR regression analysis are shown in Figure 4 and Table 7.

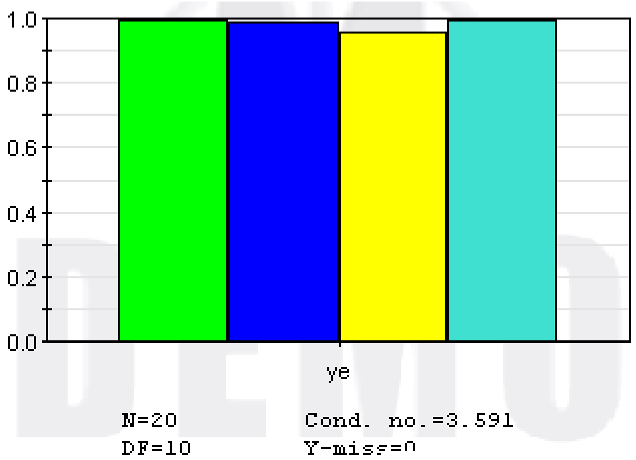
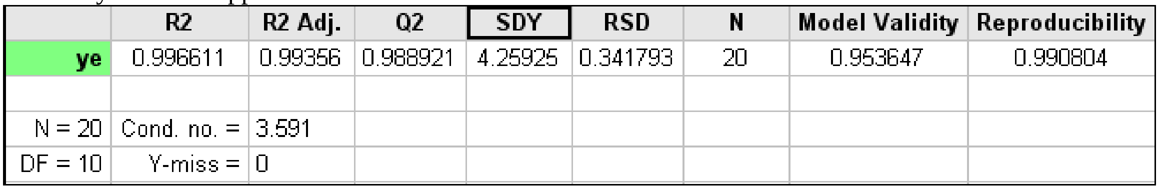


Figure 4. Statistical indicators for approximating MLR

🟨 - R^2, 🟦 - Q^2, 🟨 - model validity, 🟦 - reproducibility of the model

Table 7. Summary of MLR approximations



	R2	R2 Adj.	Q2	SDY	RSD	N	Model Validity	Reproducibility
ye	0.996611	0.99356	0.988921	4.25925	0.341793	20	0.953647	0.990804
N = 20	Cond. no. =	3.591						
DF = 10	Y-miss =	0						

The analysis of the numbers of MLR approximations leads to the following conclusions:

- The coefficients of determination R^2= 0.996611 demonstrate that among the independent variables x_1,x_2,x_3 there is almost complete determination (R^2=1). This fact was also confirmed by the adjusted coefficient of determination R^2_{Adj} = 0.99356 resulted through the formula:

$$R^2_{adj} = R^2 - \frac{p-1}{n-p}\left(1-R^2\right)$$

- Corrected fraction of the estimated response, Q^2= 0.988921 was calculated by the following equation:

$$Q^2 = 1 - \frac{PRESS}{SS}$$

(PRESS is the sum of the squares tailings, and SS is the sum of squares of the estimated values of y_e that have been adjusted using the average value, indicating a module with a very good predictive power.)

- Standard deviation, SDY, having an acceptable value of 4.25925, and a small residual standard deviation RSD = 0.341793, confirm that the analyzed model was chosen correctly.

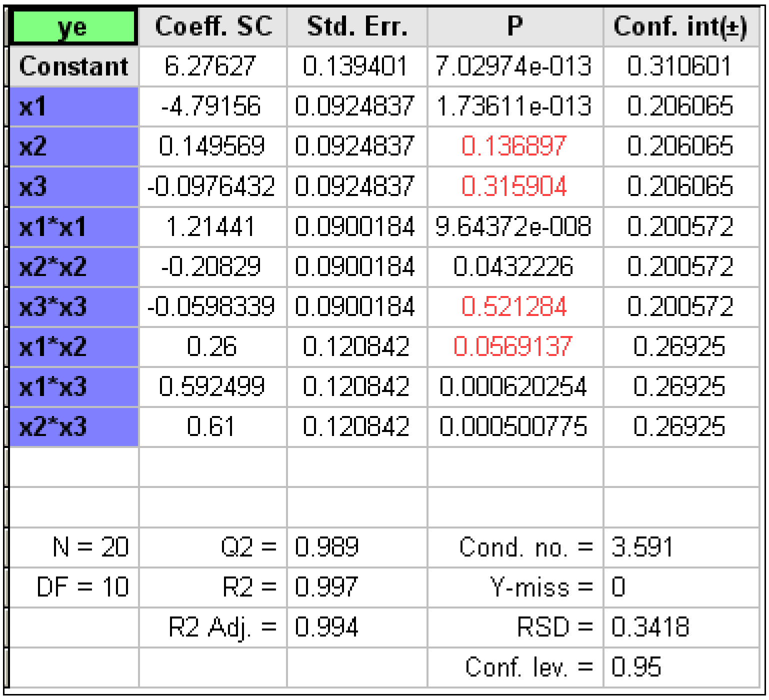
The calculated values for the coefficients of the model, for a 95% confidence interval are presented in Table 8.

Checking the significance of the regression equation coefficients was achieved through the use of confidence intervals "conf.int". The significance was verified by comparing absolute values of coefficients with the value of confidence intervals:

$$|b_j|>|\text{conf. int}|$$

The coefficients that allow the above inequality to be true are considered significant. From the data shown in Table 8, we conclude that x_2, x_3, x_3^2 and x_1x_2 and the inequality condition is not fulfilled and therefore the coefficients b_2, b_3, b_{33} and b_1b_2 are insignificant and are excluded from the regression equation.

Table 8. Model coefficients



ye	Coeff. SC	Std. Err.	P	Conf. int(±)
Constant	6.27627	0.139401	7.02974e-013	0.310601
x1	-4.79156	0.0924837	1.73611e-013	0.206065
x2	0.149569	0.0924837	0.136897	0.206065
x3	-0.0976432	0.0924837	0.315904	0.206065
x1*x1	1.21441	0.0900184	9.64372e-008	0.200572
x2*x2	-0.20829	0.0900184	0.0432226	0.200572
x3*x3	-0.0598339	0.0900184	0.521284	0.200572
x1*x2	0.26	0.120842	0.0569137	0.26925
x1*x3	0.592499	0.120842	0.000620254	0.26925
x2*x3	0.61	0.120842	0.000500775	0.26925
N = 20	Q2 =	0.989	Cond. no. =	3.591
DF = 10	R2 =	0.997	Y-miss =	0
	R2 Adj. =	0.994	RSD =	0.3418
			Conf. lev. =	0.95

Revision of model was developed by NOVA method [10], which analyzes the standard deviations of regression (model) and standard deviations of the residues.

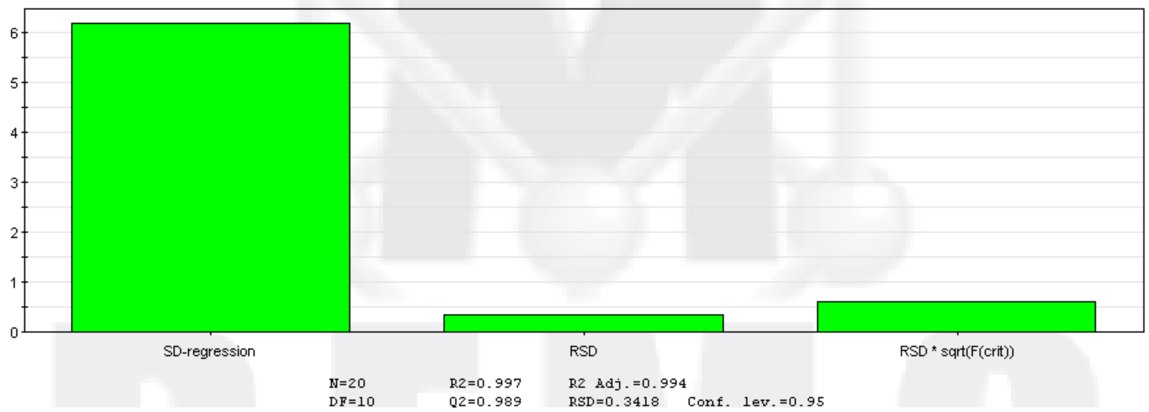
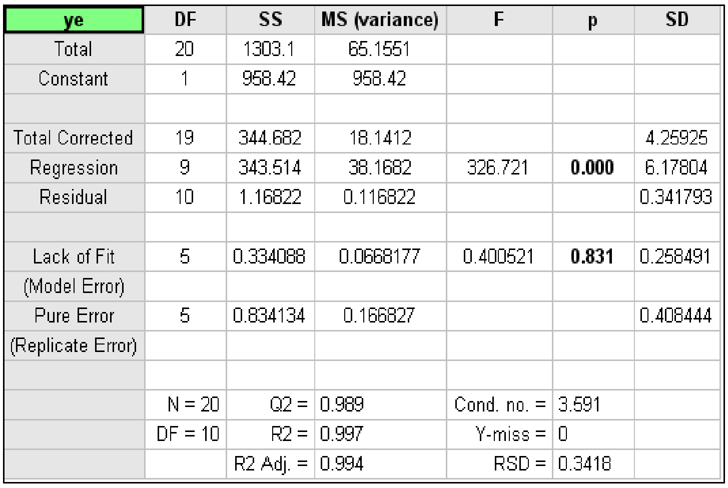


Figura 5. ANOVA diagram

There is a first bar in the ANOVA diagram (Figure 5) which represents the standard deviation of regression, and which is much higher than the third bar, the standard deviation of the residue over the upper limit of confidence interval. This confirms the correct choice of analysis of the model.

Table 9 contains the value of F test which, when compared to the corresponding critical value, contains quintiles of the distribution F (r-1, n-r), freedom degrees and they lead to the conclusion that the model is valid because the proportion of the version explained by the model is significant.

Table 9. ANOVA statistical data



ye	DF	SS	MS (variance)	F	p	SD
Total	20	1303.1	65.1551			
Constant	1	958.42	958.42			
Total Corrected	19	344.682	18.1412			4.25925
Regression	9	343.514	38.1682	326.721	**0.000**	6.17804
Residual	10	1.16822	0.116822			0.341793
Lack of Fit	5	0.334088	0.0668177	0.400521	**0.831**	0.258491
(Model Error)						
Pure Error	5	0.834134	0.166827			0.408444
(Replicate Error)						
	N = 20	Q2 =	0.989	Cond. no. =	3.591	
	DF = 10	R2 =	0.997	Y-miss =	0	
		R2 Adj. =	0.994	RSD =	0.3418	

The interpretation of the coefficients was made through the diagram of the coefficients shown in Figure 6, in which the size of the bars represent the variation of a factor encoded by 0-1 while others are maintained on average. Normalized coefficients are coefficients reported to standard deviations.

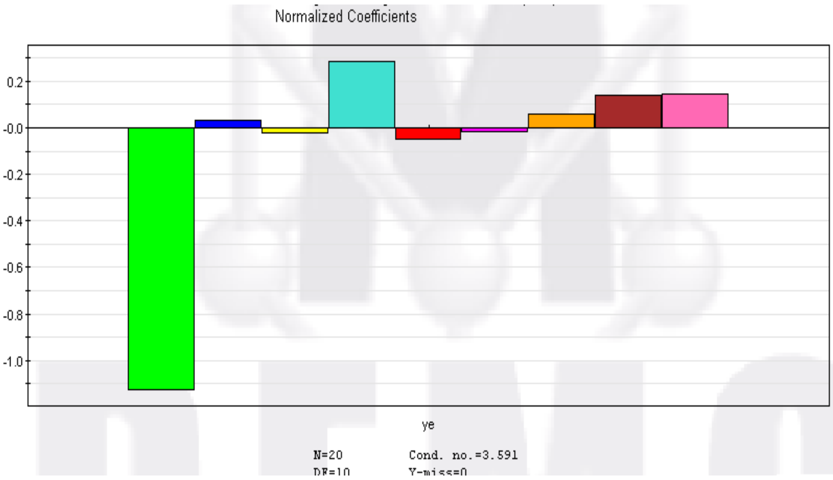


Figure 6. The diagram of the coefficients

Based on the coefficients from above it was concluded that the mathematical model of coagulation/flocculation/pre-oxidation of Prut water is described through the equation:

$$ye = 6{,}27627 - 4{,}79156x_1 + 1{,}21441x_1^2 - 0{,}20829x_2^2 + 0{,}592499x_1x_3 + 0{,}61x_2x_3$$

The following information results by analyzing the coefficients of the mathematical model in the field of values of the factors taken into account:

- the concentration of the reagent y_e influences the coagulation process 3.94 times stronger than x_1^2;
- the turbidity y_e decreases as x_1 increases;
- the increase of x_2^2 leads to turbidity decrease (favorable influence):
- the interactions between x_1x_3 and x_2x_3 influence the turbidity increase (negative effect).

This information is outlined in Figure 7, which graphically presents the intensity of the effects on turbidity of the factors encoded x_1, x_2, x_3.

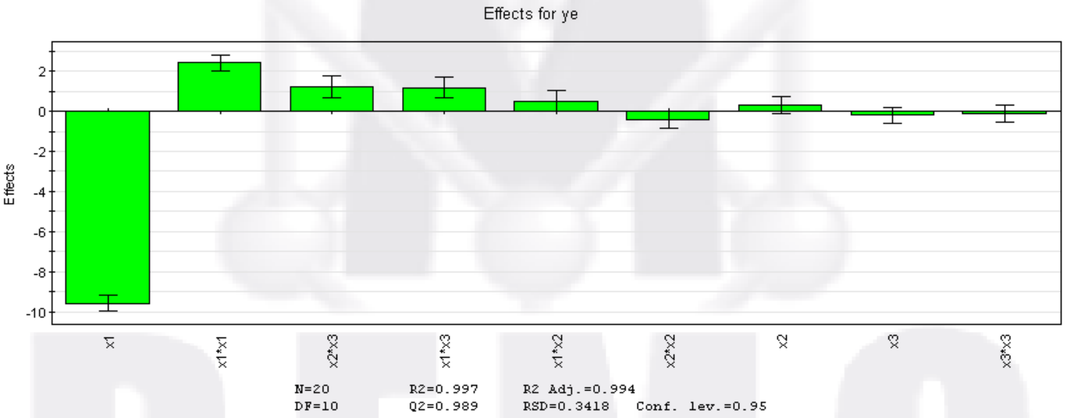


Figure 7. The Intensity of the effects of the factors upon ye

Validation of the model was achieved through analyzing the correspondence between experimental and calculated (estimated) data that are shown in Figure 8, which shows that in both situations the turbidity value is very close and thus validates the correct choice of model.

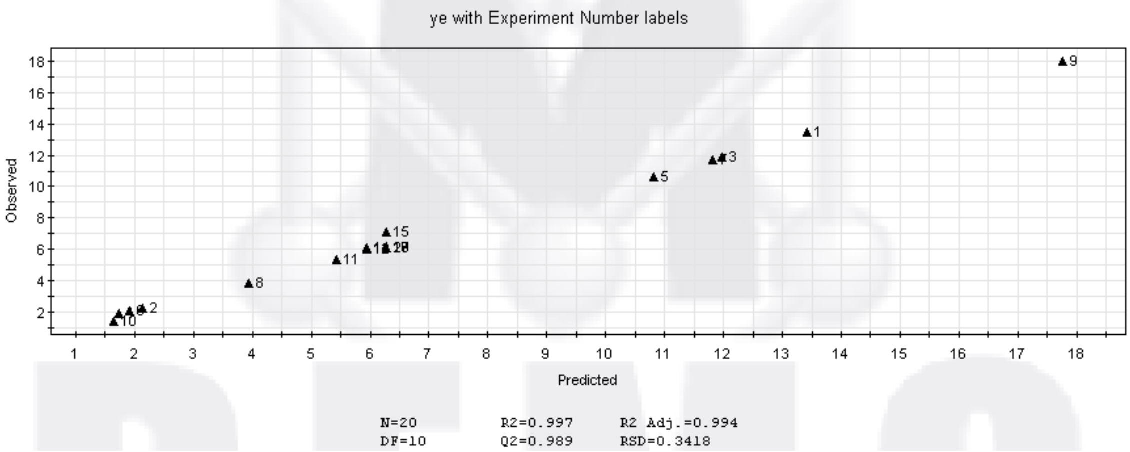
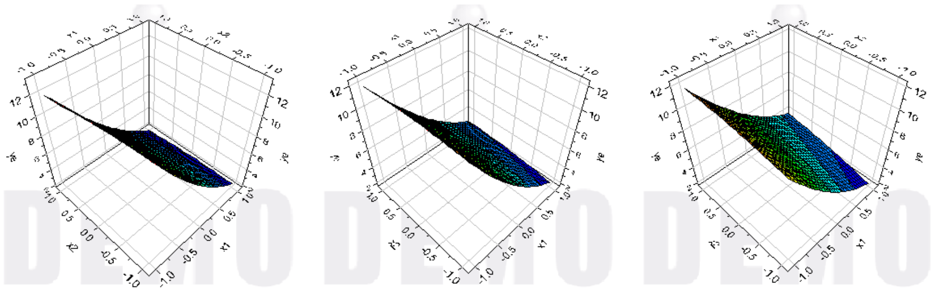


Figure 8. Correlation between experimental and calculated (estimated) y_e values

Further on, the validated model was used for prediction in order to determine the optimal conditions for achieving coagulation/flocculation/pre-oxidation.

In order to predict the influences upon y_e of independent variables and their interactions, the response surfaces and corresponding contour lines have been mapped. Each time, one factor of known value was maintained constant (coded -1, 0, 1) while the other two factors were modified. The results are shown in Figure 9 and 10.



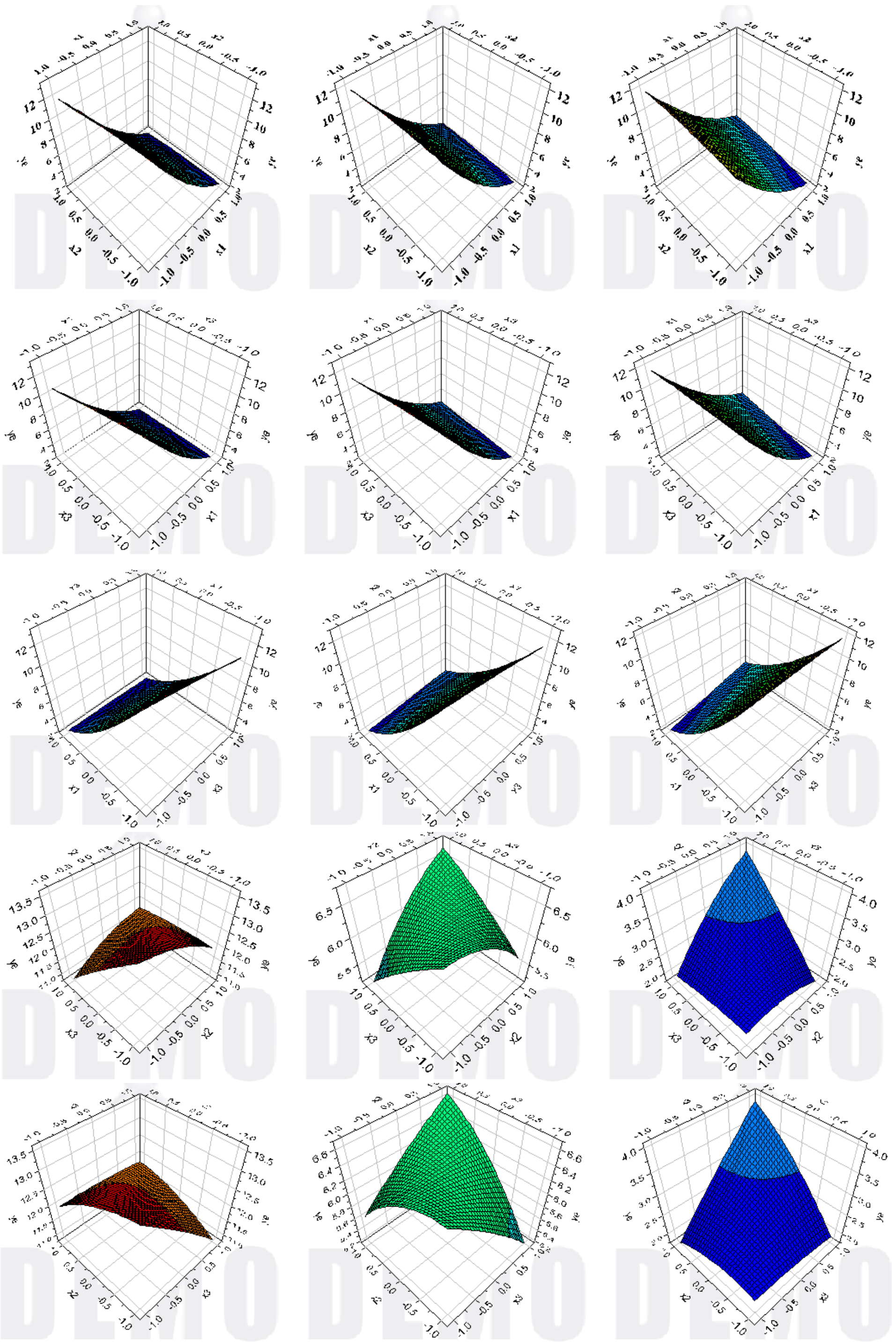
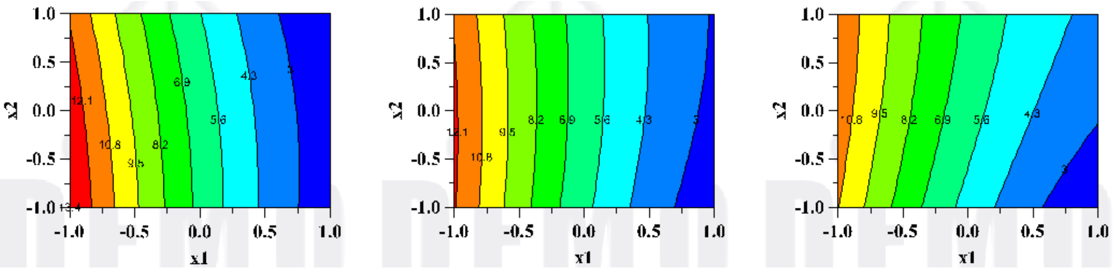


Figure 9. Response Surfaces



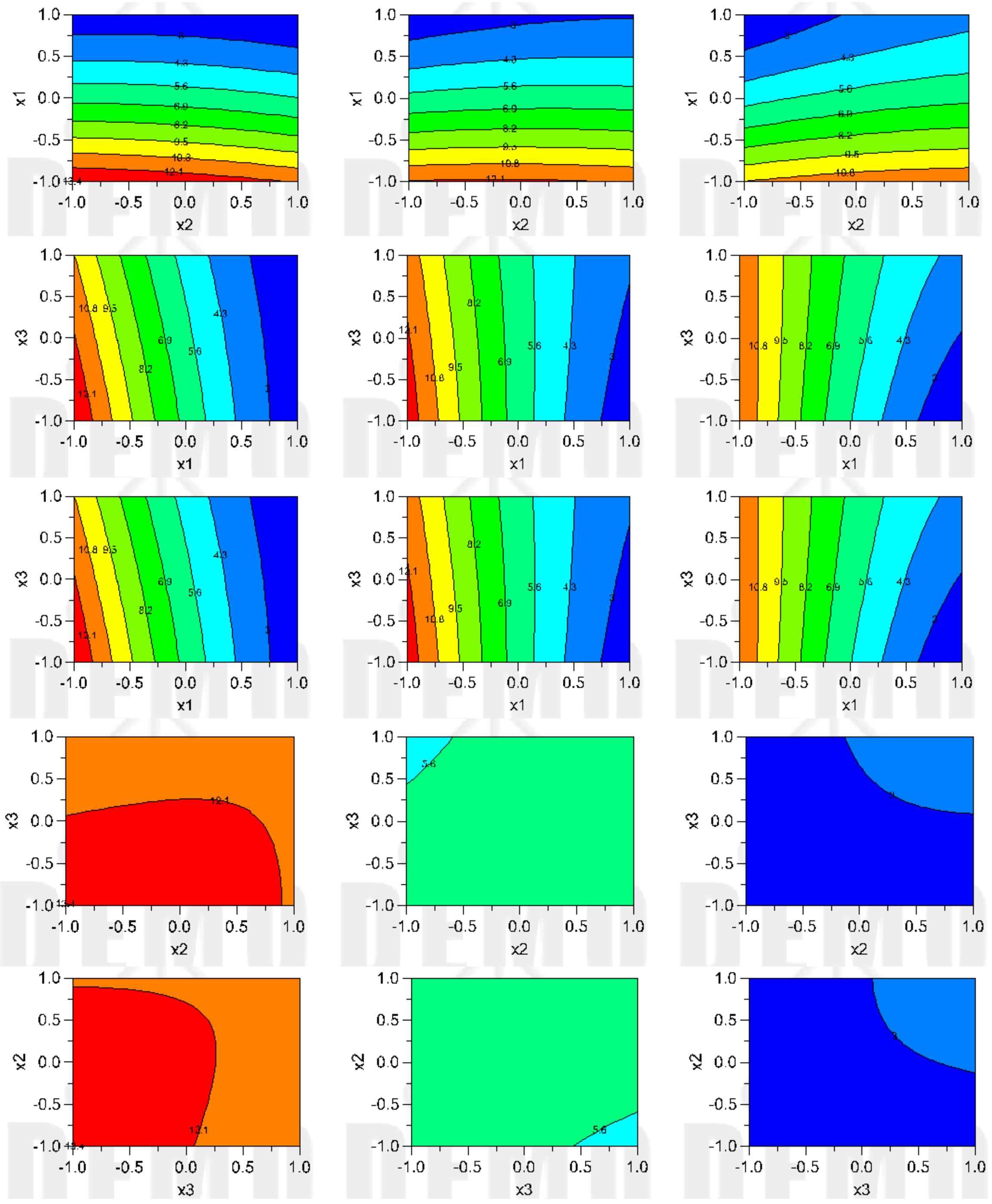
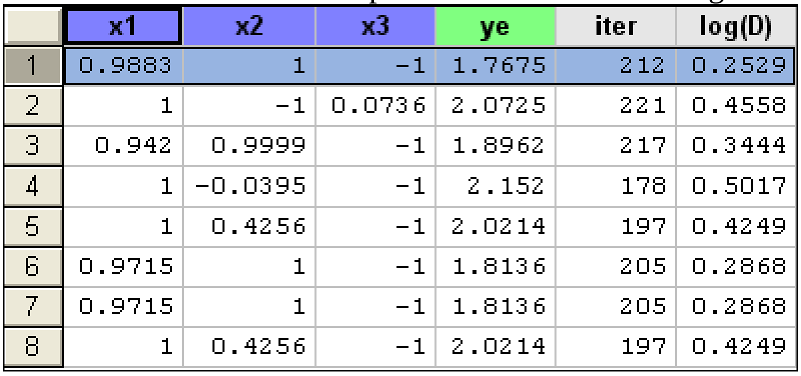


Figure 10. Level curves

Optimizing the equation that describes the performance of coagulation/flocculation/pre-oxidation processing of Prut water was achieved through the minimizing of turbidity (ye), which was carried out using MODE application and descending simplex method. Solving the optimization problem was achieved in three different ways:

a) optimization without starting values when those are generated by default MODE application. The results are presented in Table 10. Under these conditions, the minimum was obtained after 212 iterations. The best value for y_e is 1.7675, and the values of decision variables that lead to optimal y_e are x_1 = 11.25 mg·L^{-1}, x_2 = 0.5 mg·L^{-1} and x_3 = 0.1 mg·L^{-1}.

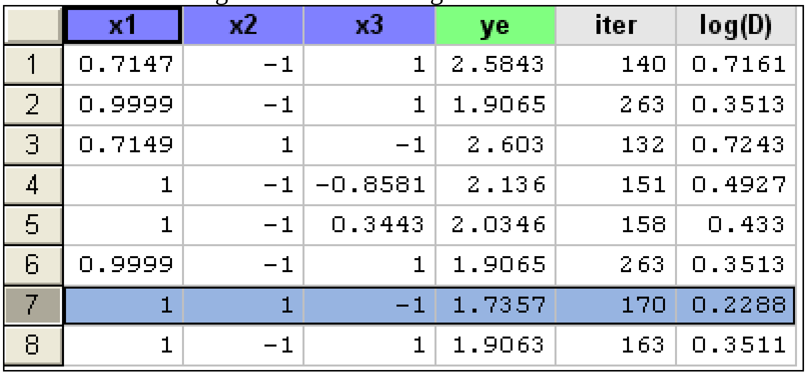
Table 10. The results of optimization without starting values



	x1	x2	x3	ye	iter	log(D)
1	0.9883	1	-1	1.7675	212	0.2529
2	1	-1	0.0736	2.0725	221	0.4558
3	0.942	0.9999	-1	1.8962	217	0.3444
4	1	-0.0395	-1	2.152	178	0.5017
5	1	0.4256	-1	2.0214	197	0.4249
6	0.9715	1	-1	1.8136	205	0.2868
7	0.9715	1	-1	1.8136	205	0.2868
8	1	0.4256	-1	2.0214	197	0.4249

b) Optimization with the automatic generation of starting values led to the results presented in Table 11. The minimum value of y_e = 1.7357 was obtained after 170 iterations when the values of decision variables were x_1 = 12.5 mg·L^{-1}, x_2 = 0.5 mg·L^{-1}, x_3 = 0.1 mg·L^{-1} corresponding to the coded values: 1, 0 and -1.

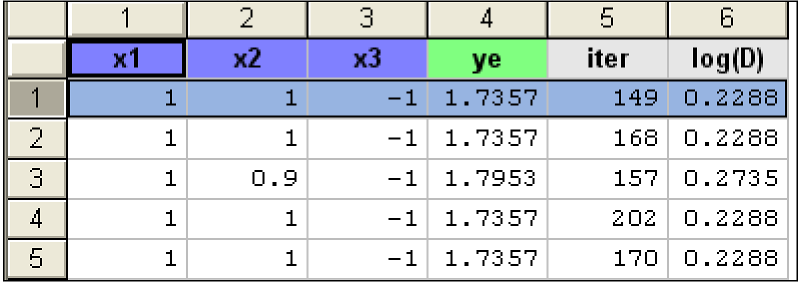
Table 11. Optimization with the automatic generation of starting values



	x1	x2	x3	ye	iter	log(D)
1	0.7147	-1	1	2.5843	140	0.7161
2	0.9999	-1	1	1.9065	263	0.3513
3	0.7149	1	-1	2.603	132	0.7243
4	1	-1	-0.8581	2.136	151	0.4927
5	1	-1	0.3443	2.0346	158	0.433
6	0.9999	-1	1	1.9065	263	0.3513
7	1	1	-1	1.7357	170	0.2288
8	1	-1	1	1.9063	163	0.3511

c) Optimization with the automatic generation of selected starting values led to the results presented in Table 12. Those values were obtained after 149 iterations.

Table 12. Optimization with the automatic generation of selected starting



	1	2	3	4	5	6
	x1	x2	x3	ye	iter	log(D)
1	1	1	-1	1.7357	149	0.2288
2	1	1	-1	1.7357	168	0.2288
3	1	0.9	-1	1.7953	157	0.2735
4	1	1	-1	1.7357	202	0.2288
5	1	1	-1	1.7357	170	0.2288

The optimization studies of the equation that describes the process of coagulation/ flocculation/pre-oxidation of Prut river water demonstrated that a 1.7357 NTU water turbidity is achieved when the following values for the decision variables are used:

- anticoagulant reagent – 12.5 mg·L^{-1} iron (III) chloride;
- flocculation reagent - 0.5 mg·L^{-1} polyacrylamide;
- pre-oxidation reagent - 0.1 mg·L^{-1} chlorine dioxide.

Practical experimentation was performed using these values, and a 1.81 NTU turbidity was obtained. This value confirmed that the model and the values obtained for independent variables using the optimized equation that describes the model were chosen correctly.

Conclusion

Modeling was done by coagulation/flocculation/pre-oxidation of Prut river water, using MODE software equation, and the parameters with major influence on the turbidity were established.

Optimization of the equation of the model was developed through minimizing turbidity values using the descending simplex method by MODE application, and the obtained values for turbidity and independent variables were validated by experiment optimized values.

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