Appendix A. Design of experiments: OFAT and CCD

The experimental design for the coagulation diagrams is shown in Table A.1. Graphical representation of the classical CCD experimental points is shown in Figure A.1.

Table A.1. Coagulation diagram experimental setup

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Al2O3**  **(mg L-1)** | **Initial pH** | | | | | | |
| 5.5 | 6.0 | 6.3 | 6.6 | 7.0 | 7.5 | 8.0 |
| 2.60 | *J01* | *J13* | *J25* | *J37* | *J49* | *J61* | *J73* |
| 3.25 | *J02* | *J14* | *J26* | *J38* | *J50* | *J62* | *J74* |
| 3.90 | *J03* | *J15* | *J27* | *J39* | *J51* | *J63* | *J75* |
| 4.55 | *J04* | *J16* | *J28* | *J40* | *J52* | *J64* | *J76* |
| 5.20 | *J05* | *J17* | *J29* | *J41* | *J53* | *J65* | *J77* |
| 5.85 | *J06* | *J18* | *J30* | *J42* | *J54* | *J66* | *J78* |
| 6.50 | *J07* | *J19* | *J31* | *J43* | *J55* | *J67* | *J79* |
| 7.15 | *J08* | *J20* | *J32* | *J44* | *J56* | *J68* | *J80* |
| 7.80 | *J09* | *J21* | *J33* | *J45* | *J57* | *J69* | *J81* |
| 8.45 | *J10* | *J22* | *J34* | *J46* | *J58* | *J70* | *J82* |
| 9.10 | *J11* | *J23* | *J35* | *J47* | *J59* | *J71* | *J83* |
| 10.4 | *J12* | *J24* | *J36* | *J48* | *J60* | *J72* | *J84* |



Figure A.1. Classical CCD for two variables, X1 and X2, distributed into three spatial components: four square vertices (red rings), which describe the variable interactions; four axial points (blue rings), which define the response surface curvature as quadratic coefficients; and four replicates of the central point (green ring), which provide a pure error estimative.

Appendix B. CCD\_A

The matrices used to obtain the six preliminary coefficients through CCD\_A are shown in Tables from B.1 to B.6.

Table B.1: Matrix X12x6

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | **x0** | **x1** | **x2** | **x12** | **x22** | **x1x2** |
|  | 1 | -1 | -1 | 1 | 1 | 1 |
|  | 1 | 1 | -1 | 1 | 1 | -1 |
|  | 1 | -1 | 1 | 1 | 1 | -1 |
|  | 1 | 1 | 1 | 1 | 1 | 1 |
|  | 1 | -1.414 | 0 | 2 | 0 | 0 |
| X12x6**=** | 1 | 1.414 | 0 | 2 | 0 | 0 |
|  | 1 | 0 | -1.414 | 0 | 2 | 0 |
|  | 1 | 0 | 1.414 | 0 | 2 | 0 |
|  | 1 | 0 | 0 | 0 | 0 | 0 |
|  | 1 | 0 | 0 | 0 | 0 | 0 |
|  | 1 | 0 | 0 | 0 | 0 | 0 |
|  | 1 | 0 | 0 | 0 | 0 | 0 |

Table B.2: The transpose of matrix X, or XT6x12

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| -1 | 1 | -1 | 1 | -1.414 | 1.414 | 0 | 0 | 0 | 0 | 0 | 0 |
| -1 | -1 | 1 | 1 | 0 | 0 | -1.414 | 1.414 | 0 | 0 | 0 | 0 |
| 1 | 1 | 1 | 1 | 2 | 2 | 0 | 0 | 0 | 0 | 0 | 0 |
| 1 | 1 | 1 | 1 | 0 | 0 | 2 | 2 | 0 | 0 | 0 | 0 |
| 1 | -1 | -1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

Table B.3: Matrix XTX6x6

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| 12 | 0 | 0 | 8 | 8 | 0 |
| 0 | 8 | 0 | 0 | 0 | 0 |
| 0 | 0 | 8 | 0 | 0 | 0 |
| 8 | 0 | 0 | 12 | 4 | 0 |
| 8 | 0 | 0 | 4 | 12 | 0 |
| 0 | 0 | 0 | 0 | 0 | 4 |

Table B.4: The inverse of XTX6x6, or (XTX)-16x6

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **0.250** | 0 | 0 | -0.13 | -0.125 | 0 |
| 0 | **0.125** | 0 | 0 | 0 | 0 |
| 0 | 0 | **0.125** | 0 | 0 | 0 |
| -0.125 | 0 | 0 | **0.156** | 0.031 | 0 |
| -0.125 | 0 | 0 | 0.031 | **0.156** | 0 |
| 0 | 0 | 0 | 0 | 0 | **0.250** |

Table B.5: Matrix XTy6x1

|  |
| --- |
| 51.9 |
| -4.6 |
| -6.4 |
| 29.5 |
| 60.3 |
| -10.9 |

Table B.6: Matrix *b*6x1. containing the second order model coefficients

|  |
| --- |
| 1.75 |
| -0.571 |
| -0.799 |
| 0.0063 |
| 3.86 |
| -2.73 |

Aiming to verify whether all coefficients are relevant and necessary, the variances may be estimate by using MSResidual when the model does not present lack-of-fit, or using MSLack-of-fit when the model present lack-of-fit. Actually, both MS may be tested in order to achieve the best agreement with the real data. Each individual variance is obtained multiplying the main diagonal of the matrix (XTX)-1 (Figure B.4) by each MS, and the errors (standard deviation) are easily deduced. At the present case, MSResidual provides the more appropriate ANOVA (Table B.2) even with an initial lack-of-fit. A Student's *t* test for the 6 coefficients implies a critical *t* value of 2.571 (DF = 5, p = 0.05) and the confidence interval (CI) for each coefficient is the product between the errors and the *t* value; if the coefficient ± CI value encompasses the zero, there is no significance and the coefficient must be removed from the model (Figure B.1).

Table B.7. Initial significance evaluation for the CCD\_Aa coefficients

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Coefficient** | | **SDb (XTX)-1** | **Variance** | **Error** | **DFc (t)** | **CId** | **Significant** |
| b0 | 1.75 | 0.250 | 0.34463 | 0.58705 | 5 | 1.509 | YES |
| b1 | -0.571 | 0.125 | 0.17234 | 0.41514 |  | 1.067 | NO |
| b2 | -0.799 | 0.125 | 0.17234 | 0.41514 |  | 1.067 | NO |
| b11 | 0.0063 | 0.156 | 0.21540 | 0.46411 |  | 1.193 | NO |
| b22 | 3.86 | 0.156 | 0.21540 | 0.46411 | tcritical | 1.193 | YES |
| b12 | -2.73 | 0.250 | 0.34463 | 0.58705 | 2.571 | 1.509 | YES |
| *CCD\_A: central composite design A; bSD: standard deviation; cDF: degree of freedom; dCI: confidence interval* | | | | | | | |



Figure B.1. CCD\_A coefficients and their respective confidence intervals.

Thus, the optimized matrix X (12x3) was constructed only with the significant coefficients (b0, b22, and b12), as well as the derived matrices XTX3x3, (XTX)-13x3, XTy3x1 e *b*3x1 with help of the Bluebit online matrix calculator.

Table B.8. Optimized matrix X (12x3)

|  |  |  |  |
| --- | --- | --- | --- |
|  | **b0** | **b22** | **b12** |
|  | 1 | 1 | 1 |
|  | 1 | 1 | -1 |
|  | 1 | 1 | -1 |
|  | 1 | 1 | 1 |
|  | 1 | 0 | 0 |
| X12x3 = | 1 | 0 | 0 |
|  | 1 | 2 | 0 |
|  | 1 | 2 | 0 |
|  | 1 | 0 | 0 |
|  | 1 | 0 | 0 |
|  | 1 | 0 | 0 |
|  | 1 | 0 | 0 |

Table B.9. Optimized matrices XTX (3x3). XTy (3x1) e *b* (3x1)

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | 12 | 8 | 0 |  | 0.15 | -0.1 | 0 |  | 51.9 |  | 1.76 |
| XTX3x3: | 8 | 12 | 0 | (XTX)-13x3: | -0.1 | 0.15 | 0 | XTy3x1: | 60.3 | *b*3x1: | 3.86 |
|  | 0 | 0 | 4 |  | 0 | 0 | 0.25 |  | -10.9 |  | -2.73 |

Regarding the amount of information that can be explained, analysis based on the sum of squares (SS) provides the R2 parameters. R2 is the percentage of the total SS that is related to the regression model SS. For instance, CCD\_A present R2 = 0,9429. If there were no data to estimate the pure error SS (replicates of CCD central point), the maximum explained percentage would be Rmax = 0.9994. After the optimization, CCD\_A presented R2 = 0.8896 and R2max = 0.8934. In spite of the lower R values after the optimization, it is possible to say the model is still consistent based on the analysis of F factors.

Therefore, it is possible simulated the residual turbidity through optimized CCD\_A.

Table B.10. Residual turbidity values predicted by optimized CCD\_A .

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  | pH (encoded) | | | | | | | |  |  |
|  |  | -1.414 | -1.010 | -0.606 | -0.202 | 0.202 | 0.606 | 1.010 | 1.414 |  |  |
| Coagulant (values) | 0.0 | 4.0 | 5.6 | 7.1 | 8.7 | 10.3 | 11.8 | 13.4 | 14.9 | -1.414 | Coagulant (encoded) |
| 0.7 | 1.8 | 2.9 | 4.0 | 5.1 | 6.3 | 7.4 | 8.5 | 9.6 | -1.010 |
| 1.3 | ***0.8*** | ***1.5*** | 2.2 | 2.8 | 3.5 | 4.2 | 4.8 | 5.5 | -0.606 |
| 2.0 | ***1.1*** | ***1.4*** | 1.6 | 1.8 | 2.0 | 2.3 | 2.5 | 2.7 | -0.202 |
| 2.7 | 2.7 | 2.5 | 2.3 | 2.0 | 1.8 | 1.6 | ***1.4*** | ***1.1*** | 0.202 |
| 3.4 | 5.5 | 4.8 | 4.2 | 3.5 | 2.8 | 2.2 | ***1.5*** | ***0.8*** | 0.606 |
| 4.0 | 9.6 | 8.5 | 7.4 | 6.3 | 5.1 | 4.0 | 2.9 | 1.8 | 1.010 |
| 4.7 | 14.9 | 13.4 | 11.8 | 10.3 | 8.7 | 7.1 | 5.6 | 4.0 | 1.414 |
|  |  | 7.8 | 8.0 | 8.2 | 8.4 | 8.6 | 8.8 | 9.0 | 9.2 |  |  |
|  |  | pH (values) | | | | | | | |  |  |

Appendix C. CCD\_B

The surface response and simulation with a dataset is presented.

The preliminary algebraic model obtained is presented in Equation (C.1), and the optimized model (with the significant coefficients only) can be shown in Equation (C.2).

|  |  |  |  |
| --- | --- | --- | --- |
| |  |  | | --- | --- | |  |  | | (C.1) |
|  |  |
|  | (C.2) |
| (± 2.071) |  |

The surfaces obtained when Equation C.1 is used can be seen in figures C.1. and C.2. Figures C.3 and C.4 are simulations based on Equation C.2.

3D surface coded.tif

Figure C.1. Three-dimensional response (surface) for the CCD\_B (all coefficients)

|  |  |
| --- | --- |
| 2D experimental data - coded.tif | Contour experimental data - coded.tif |

Figure C.2. Two-dimensional response (contour surface) for the CCD\_B (all coefficients)

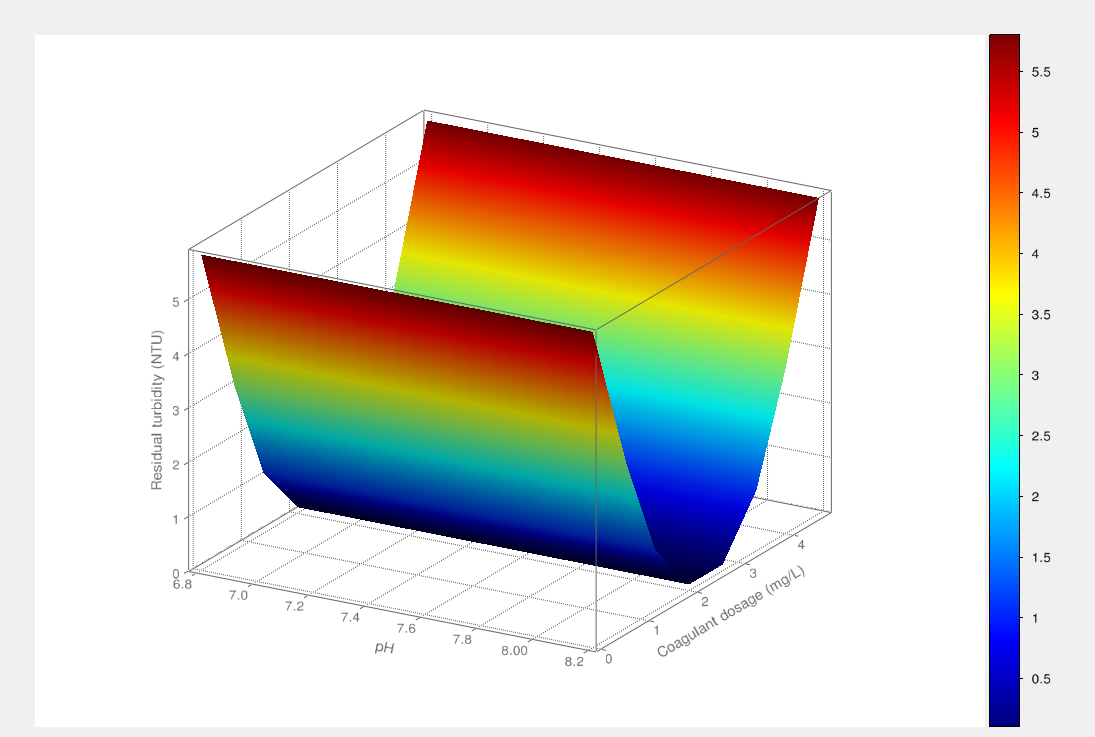


Figure C.3. Simulation of three-dimensional response (surface) for the CCD\_B, using equation C.2

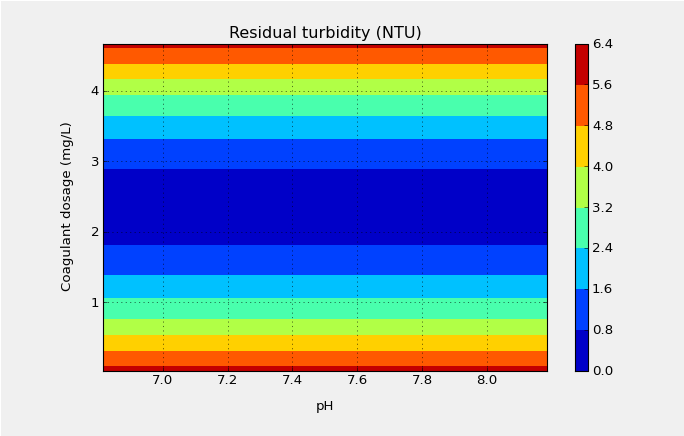


Figure C.4. Simulation of contour plot for the CCD\_B, using equation C.2

Appendix D. CCD\_C

The 2D response surface for CCD\_C is shown.

|  |  |
| --- | --- |
| 2D surface.tif | Contour plot.tif |

Figure D.1. Two-dimensional response (contour surface) for the CCD\_C

Appendix E. Response surface for CCD\_D.

3D surface - only significant coefficients.tif

Figure E.1. Three-dimensional response (surface) for the CCD\_D (only for significant coefficients)

|  |  |
| --- | --- |
| 2D surface - only significant coefficients.tif | Contour plot - only significant coefficients.tif |

Figure E.2. Two-dimensional response (contour surface) for the CCD\_D (only for significant coefficients).