QUALITY ASSESSMENT OF THE ALUMINIUM SULPHATE
COAGULANT RECOVERED FROM METALLURGICAL
SLAG BASED ON A CORRELATION OF THE REMOVED
PHOSPHOROUS FROM MUNICIPAL WASTEWATERS

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The presence of excess phosphorus in the effluent discharged to natural
water bodies is the cause of algal blooms and eutrophication. A special care to
secondary aluminium slag is necessary for preventing the environment pollution and
for recovering valuable materials. The lab-scale tests for phosphorus removal from
municipal wastewaters have been performed by using the commercial vs. recovered
aluminium sulphate (AS) from different sorts of slags coming from metallurgical
units of Romania. The data treatment, and derivation of a statistical nonlinear
correlation model indicate comparable efficiency of AS-recovered product vs. AS-
commercial product, and a decline of the removed P / dose mass vs. the used
coadulant dose.

Keywords: municipal wastewater, phosphorus removal, aluminum sulphate (AS),
municipal slag

Nomenclature:

\begin{align*}
a, \ b & = \text{Correlation parameters} \\
D & = \text{Mass of AS based coagulant recovered from metallurgical}
\hspace{1em} \text{slag} \\
f & = \text{Estimation objective function} \\
I & = \text{Identity matrix} \\
k & = \text{Kinetic parameter vector} \\
n & = \text{Number of measured experimental points} \\
p & = \text{Number of parameters in the model} \\
r & = \text{Number of observed variables} \\
R, U & = \text{Matrices defined in equations (A4 and A5)} \\
M_{\text{RP}} & = \text{Mass of removed P} \\
s^2 & = \text{Model prediction variance} \\
t & = \text{Student statistical distribution (eq. A6)} \\
\nu & = \text{Parameter variance-covariance matrix (see eq. A3)} \\
x & = \text{Independent variable} \\
y & = \text{Dependent variable}
\end{align*}

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1. Introduction

Eutrophication in water bodies has been recognised as one of the main environmental concerns in recent years. The accelerated economic development of recent years has led in turn to an acceleration of this natural process as a result of human waterside activities, which carry organic matter and nutrients (nitrogen and phosphorus, in particular) into the natural water bodies through the disposal of agricultural, municipal and industrial wastewaters. The presence of excess of phosphorus in the discharged effluent has been known to be the main cause of algal blooms and eutrophication. The average molar ratio of nitrogen, phosphorus and carbon in algal protoplasm is approximately 15:1:105. If any of these components is less than this natural ratio, it will limit the algal growth. Therefore, very small amounts of phosphorus can cause substantial algal growth and its removal is more effective compared to nitrogen for preventing eutrophication [1].

Currently, the wastewater treatment plants remove the phosphorus by adding chemicals (coagulants) to precipitate the phosphate present in the wastewater. Chemicals may be added to primary, secondary, or tertiary treatment processes. A variety of metal salts are used as coagulants in this respect. The most common chemicals are aluminum sulphate (alum, AS) and ferric chloride [2].

Aluminum ions combine with phosphate ions to form aluminum phosphate, as shown by the following reaction:

$$\text{Al}^{3+} + \text{PO}_4^{3-} \rightarrow \text{AlPO}_4 \downarrow$$

A range of factors, such as the nature of water, the coagulation pH, and the dose of coagulant influence the range of species formed and subsequently, the treatment performance. The optimum pH for phosphorus removal using alum falls in the range of 5.5 – 6.5 [3].

The aim of this paper is to evaluate the coagulation performance of a large number of aluminum sulphate products recovered from metallurgical slags vs. the AS-commercial product based on a phosphorus removal index. The phosphorous removal efficiency was tested by using municipal wastewaters from various
sources, being then statistically correlated with a nonlinear model with the employed AS dose.

2. Aluminum sulphate recovered from metallurgical slag

Today the aluminium is produced via two different ways: primary aluminium production from bauxite ore, and secondary aluminium production by recycling aluminium from process scraps and from aluminium-based products.

Secondary aluminium is also known as recycling aluminium. All aluminium products can be recycled after use. Recycling of aluminium is extremely important due to several economic and environmental reasons. In addition to this, aluminium is recovered from slag and salt cake [4]. The scrap feed, which is a complex combination of all types of aluminium scrap collected, is loaded into melting furnaces.

Industrial production of secondary aluminium generates annually large amounts of slag (black slag and salt cake), which has a variety of chemical and mineralogical composition. The type and quality of the slag is determined by the method of melting, the raw material, the temperature and mixing conditions, etc.

The resulted wastes from the metallurgical process contain hazardous chemicals, such as metallic oxides, alloys, chlorides, fluorides, nitrites, carbides, sulphides etc. [5].

The disposal of slag is a worldwide problem. Its leachability can lead to the transport of toxic metal ions into ground water, and its high reactivity with water or even humidity in air leads to the formation of toxic, harmful, explosive, poisonous and unpleasant odorous gases, such as NH₃, CH₄, PH₃, H₂ and H₂S. These gaseous emissions from the slag that result from contact with pluvial water are, consequently, of great environmental concern [6, 16].

It is therefore fully justified the removal of wastes present in the secondary aluminium industry sites in order to ensure protection of the environment and the introduction into the economic circuit of recyclable materials [15]. Typically, black slag contains 10-20 wt% aluminium metal. The non-metallic residue (salt cake) produced from scarp smelting operations contains residual metallic aluminium in a 5-7 wt% content [7].

The processing of aluminium slag involves screening operations, washing with / without simultaneous grinding, drying and disintegration to remove soluble salts. The method used for the recovery of aluminium sulphate is chemical and hydrometallurgical treatment of the waste in acid medium for a quantitative bring of aluminium in the solution, followed by evaporation and crystallization processes of the solution [8, 17].
3. Experimental section

To test the use of recovered aluminium sulphate (AS) for removal of phosphorus from wastewater, a lab-scale experimental program has been developed by employing as tests municipal wastewaters from various sources. Both commercial AS and recovered AS have been used as coagulants, the recovered AS being obtained from different varieties of slag coming from small and medium foundries of Romania. The used municipal wastewaters have been sampled from the general collector of Bucharest city and Pitești city.

The following substances were used for the present study: aluminium sulphate Kemira-white (SR EN 878:2004, Kemwater Cristal Comp.) with 9,0 ±0,2% aluminium content; AS-based products of lab-scale prepared [8, 17] with an aluminium content of 5,2 - 9,3%; other p.a. reagents are commonly used by the standard water quality analysis below listed. The prepared working solutions are of 10% concentration as required by the chemical treatment step of wastewater in the common wastewater treatment plants.

Standard methods of analysis have been employed to determine the water quality parameters, that are the phosphorous [9,18] and pH [10].

Optimal mineral salt dose depends on the wastewater type, and it can be expected to vary with the characteristics of each treated wastewater. To simulate the lab-scale coagulation capability of recovered AS, the standard Jar-test was employed [11]. Based on this procedure, the minimum coagulant dose necessary to obtain the adequate level of treatment and optimum working pH (pH = 5.5-6.5) were established.

The wastewater sample (of 1 L volume) was introduced into a reaction vessel (of 2 L) and mixed with the aluminium salt under rapid mechanical stirring (n = 160 rot/min) for 2 minutes to ensure a uniform dispersion of the chemical.

The correction of pH to get the optimum value was made by using sodium hydroxide solution. A small quantity of anionic polymer was then mixed slowly (40 rot/min) for longer time (20 minutes) to assist in the agglomeration and settling of the metal-phosphate flocks.

The resulted chemically treated water was transferred in Imhoff cones to determine the separation curves, volumes and basic characteristics of the resulted chemical sludge. Besides, additional tests have been performed to determine the treated water quality and the phosphorus removal efficiency when using commercial AS and recovered AS from various slag sources.

4. Results and Discussions

Experiments for testing the AS-based coagulant product obtained by the mentioned technology from the metallurgical slag are performed by using municipal wastewaters from various sources. Among the check water quality
tests, this study is focused on the coagulant capacity of removing the phosphorous from water. The measured initial and residual value of the phosphorous content in each tested wastewater are presented in Table 1 together with the applied coagulant dose and for every AS-product number (P1…P30) obtained from different metallurgical slag sources.

*Table 1*

<table>
<thead>
<tr>
<th>The recovered AS product no.</th>
<th>Coagulant dose (D)</th>
<th>Phosphorous (mg/L)</th>
<th>Rel. removed phosphorous (RRP)</th>
<th>Phosphorous (mg P/mg dose)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg/L</td>
<td>mg Al(3+)/L</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wastewater # 1 (Initial load)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>The blank lab sample</td>
<td>300</td>
<td>24.3</td>
<td>0.43</td>
<td>0.0248</td>
</tr>
<tr>
<td>P1</td>
<td>300</td>
<td>27.6</td>
<td>0.44</td>
<td>0.0247</td>
</tr>
<tr>
<td>P2</td>
<td>300</td>
<td>28.2</td>
<td>0.45</td>
<td>0.0247</td>
</tr>
<tr>
<td>P3</td>
<td>300</td>
<td>24.6</td>
<td>0.29</td>
<td>0.0252</td>
</tr>
<tr>
<td>P4</td>
<td>300</td>
<td>21.9</td>
<td>0.20</td>
<td>0.0255</td>
</tr>
<tr>
<td>P5</td>
<td>300</td>
<td>27.9</td>
<td>0.21</td>
<td>0.0255</td>
</tr>
<tr>
<td>P6</td>
<td>300</td>
<td>22.5</td>
<td>0.27</td>
<td>0.0253</td>
</tr>
<tr>
<td>P7</td>
<td>300</td>
<td>24.3</td>
<td>0.24</td>
<td>0.0254</td>
</tr>
<tr>
<td>Wastewater # 2 (Initial load)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>The blank lab sample</td>
<td>100</td>
<td>8.1</td>
<td>0.60</td>
<td>0.0537</td>
</tr>
<tr>
<td>P1</td>
<td>100</td>
<td>9.2</td>
<td>0.52</td>
<td>0.0545</td>
</tr>
<tr>
<td>P2</td>
<td>100</td>
<td>9.4</td>
<td>0.58</td>
<td>0.0539</td>
</tr>
<tr>
<td>P3</td>
<td>100</td>
<td>8.2</td>
<td>0.58</td>
<td>0.0539</td>
</tr>
<tr>
<td>P4</td>
<td>100</td>
<td>7.3</td>
<td>0.45</td>
<td>0.0552</td>
</tr>
<tr>
<td>P5</td>
<td>100</td>
<td>9.3</td>
<td>0.59</td>
<td>0.0538</td>
</tr>
<tr>
<td>P6</td>
<td>100</td>
<td>7.5</td>
<td>0.41</td>
<td>0.0556</td>
</tr>
<tr>
<td>P7</td>
<td>100</td>
<td>8.1</td>
<td>0.40</td>
<td>0.0557</td>
</tr>
<tr>
<td>Wastewater # 3 (Initial load)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>The blank lab sample</td>
<td>100</td>
<td>8.1</td>
<td>0.28</td>
<td>0.0682</td>
</tr>
<tr>
<td>P13</td>
<td>100</td>
<td>6.1</td>
<td>0.31</td>
<td>0.0679</td>
</tr>
<tr>
<td>P14</td>
<td>100</td>
<td>5.7</td>
<td>0.51</td>
<td>0.0659</td>
</tr>
<tr>
<td>P15</td>
<td>100</td>
<td>6.5</td>
<td>0.18</td>
<td>0.0692</td>
</tr>
<tr>
<td>P16</td>
<td>100</td>
<td>8.0</td>
<td>0.19</td>
<td>0.0691</td>
</tr>
<tr>
<td>P17</td>
<td>100</td>
<td>9.3</td>
<td>0.13</td>
<td>0.0697</td>
</tr>
<tr>
<td>Wastewater # 4 (Initial load)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>The blank lab sample</td>
<td>1000</td>
<td>81.0</td>
<td>0.040</td>
<td>0.0080</td>
</tr>
<tr>
<td>P18</td>
<td>1000</td>
<td>65.9</td>
<td>0.057</td>
<td>0.0079</td>
</tr>
</tbody>
</table>
While the applied AS-product dose varies in the range of 100-1000 mg/L, the removed phosphorous relative index varies in the range of 0.008-0.070 mg removed P / mg dose, with an average of 0.0136 and a standard deviation of 0.0220 mg P/mg, that is a quite satisfactory coagulant effectiveness. The phosphorous removal capacity has been referred to the used coagulant dose and not vs. Al$^{3+}$ content because each AS-product contains small percentages of various other salts with coagulant properties that can influence the data analysis.

Starting from the experimental data of Table 1, one tries to evaluate the coagulant effectiveness in a more accurate and theoretical way by trying to determine a statistical correlations between the applied coagulant dose (D) and resulted P-removal index (MRP = mass of removed phosphorous). Looking at the evolution of MRP as function of applied dose of coagulant, it is to remark the flattening of the curve at large doses. Consequently, by analogy with the Langmuir isothermal adsorption curve, one propose the following simple nonlinear correlation of the form:

$$MRP = a \frac{b \cdot D}{1 + b \cdot D} \quad \Rightarrow \quad \frac{1}{MRP} = \frac{1}{a} + \frac{b}{a \cdot b} \cdot \frac{1}{D}$$

(1)
where: $D =$ mass of AS based coagulant dose recovered from metallurgical slag (mg/L); $MRP =$ mass of removed P (mg removed P/L); $a,b =$ model constants, which after a variable transformation can be re-written in a linear form:

$$y = \frac{1}{MRP} = A + B \cdot x,$$

where: $A = \frac{1}{a}$, $B = \frac{1}{ab}$, $x = \frac{1}{D}$,

and $k = [A,B]$ = empirical correlation coefficient vector. Such a nonlinear correlation reduces in fact to the standard linear model $y = A + B \cdot x$, with $p = 2$ number of parameters. By applying the classical linear regression procedure with the least squares estimator $[13]$, one obtains the estimate of the parameter vector $k$ presented in Table 2. Experimental error standard deviation (noise level) was estimated from replicates obtained for the same wastewater but treated with various AS-products. Its level in the transformed variable terms is estimated at $\sigma_y \approx 0.0017 \text{ (mgP/L)}^{-1}$, the value being ca. 1% of the observed average $1/\text{average}(MRP) = 0.1434 \text{ (mgP/L)}^{-1}$, derived from Table 1 data.

The estimate statistical analysis follows the standard methodology described for instance by Maria [13], including model adequacy and estimate significance statistical tests (see Appendix and the footnotes of Table 2 [13]). Test results presented in Table 2 indicate an adequate model (in the logarithmic form), i.e. a multiple correlation coefficient around 0.85, a standard deviation of model predictions around 8% of the observed value, and a satisfactory $\chi^2$ adequacy test for 95% confidence level. The estimated parameters quality tests of Table 2 indicate all model constants as being significant, that is small 95% confidence intervals, t-tests higher than the critical value (of 95% confidence), high correlation coefficients, and values of the ridge test ($\lambda_j/\bar{\sigma}^2$) of Maria & Rippin [14] much higher than the critical threshold 1.

The residual plots presented in Fig. 1 confirm the satisfactory adequacy of the model. Indeed, the residuals are alternate positive and negative and of small values, while the predicted vs. observed $y$-plot indicate alternate values equally disposed in the vicinity of the graph diagonal. Such plots confirm the hypothesis of constant experimental noise (normally distributed), the linear character of the Log-correlation, and the absence of outliers in data [13].

As another observation, it is very interesting to observe that the removed mass of phosphorus from wastewater divided by the coagulant dose (mg P/mg AS-product dose) is exponentially decreasing with the used coagulant dose. However, in absolute terms, the mass of removed phosphorus ($MRP$) is increasing with the applied dose until a maximum is reached (the optimal dose), higher than which application of larger coagulant doses lead to a negligible increase in the removed P.
As another observation, the derived correlation model can be a very useful tool in predicting what is the optimum coagulant dose to be employed for a new treated wastewater when only the initial load with phosphorous is known, by using the transformed model (2):

\[
\frac{I}{D} = \left(\frac{1}{MRP} - A\right)B, \quad \text{valid for } MRP < 8.26 \text{ mg/L.}
\]

(3)

For instance, if one desire to predict the necessary dose to remove \( MRP = 5 \text{ mg/L} \) from a wastewater, the value of \( D \) results by solving the nonlinear equation (3), leading to \( D = 58 \text{ mg/L} \), i.e. a value never tested in the laboratory (see Table 1).

**Table 2**

Model adequacy and estimate quality tests for the correlation \( \ln(y) = a + b \cdot x \) of the data from Table 1 (standard deviation of the observed variable \( \ln(y) \) is \( \sigma = 0.05; y = \text{mg removed phosphorous} / \text{mg AS dose}; x = \text{mg AS product dose used} \))

<table>
<thead>
<tr>
<th>Adequancy test</th>
<th>Test value</th>
<th>Critical value</th>
<th>Conclusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R ) (note a)</td>
<td>0.85</td>
<td></td>
<td>Ok</td>
</tr>
<tr>
<td>( S ) (note b)</td>
<td>0.01160</td>
<td>Avg. ( y_{\text{exp}} = \bar{y} = 0.1434 )</td>
<td>Ok (ca. 8% of ( \bar{y} ))</td>
</tr>
<tr>
<td>( \chi^2 ) (note c)</td>
<td>49.2</td>
<td>( \chi^2 (n - p; 0.95) = 51 )</td>
<td>Adequate</td>
</tr>
</tbody>
</table>

Parameter | Estimate | 95% confidence | t-test | Correlation matrix | \( \lambda_j / \tilde{\sigma}^2 \) | Conclusion |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( A )</td>
<td>0.12105</td>
<td>( \pm 8.8 \cdot 10^{-4} )</td>
<td>278</td>
<td>1</td>
<td>0.84</td>
<td>7.2 \cdot 10^7</td>
</tr>
<tr>
<td>( B )</td>
<td>4.5848</td>
<td>( \pm 1.4 \cdot 10^{-1} )</td>
<td>66.5</td>
<td>0.84</td>
<td>1</td>
<td>4.5 \cdot 10^{12}</td>
</tr>
</tbody>
</table>

(a) \( R \) = multiple correlation coefficient, evaluated with the relationship:

\[
\sum_{u=1}^{n} y_i - \hat{\bar{y}}^2 = (1 - R^2) \frac{\sum_{u=1}^{n} (y_u - \bar{y})^2}{n} \; ; \; \bar{y} = (\sum_{u=1}^{n} y_i)/n ;
\]

(b) \( s^2 = \left[ y_{\text{exp}} - \hat{y}_{\text{mod}} \right]^2 / (n - p) \) = model prediction variance; \( n = 32 \) is number of experimental points; \( p = 2 \) is the number of model parameters.

(c) Calculated \( \chi^2_c = s^2 / \sigma^2 \); \( \chi^2 (df; q) \) denotes the quantile of the \( \chi^2 \)-statistics with \( df \) degree of freedom and \( q \) confidence level;  

(d) Confidence interval of the estimated parameter \( k_j \), computed with the relationship:

\[
k_j = \hat{k}_j \pm \sqrt{\left[V(\hat{k})\right]_{jj}} 1t(n - p; 0.975\%) ; \; V(\hat{k})^{-1} = \sum_{u=1}^{n} \frac{1}{\sigma_u^2} \left[ \frac{\partial y_u}{\partial k} \right]_{p}^{T} \left[ \frac{\partial y_u}{\partial k} \right]_{p,1} ;
\]

\( V = \) estimate covariance matrix; \( k = [a, b] \);  

\( t(df; q) = \) quantile of the Student-statistics with \( df \) degree of freedom and \( q \) confidence level;
(e) Student test for parameter significance:
\[
t_j = \frac{\hat{k}_j}{\sqrt{\frac{V(\hat{k})_{jj}}{n-p}} > t(n-p;97.5\%) = 2.042.
\]

(f) \( R \) is the parameter inter-correlation matrix calculated with the relationship:
\[
R(\hat{k})_{[p,p]} = \{R_{ij}\}, \quad R_{ij} = \frac{[V(\hat{k})]_{jj}}{\sqrt{[V(\hat{k})]_{ii}[V(\hat{k})]_{jj}}} \in [-1,1].
\]

(g) The parameter ‘ridge selection’ test of Maria and Rippin [14]: \( \lambda_j / \tilde{a}^2 \geq 1 - 3 \), where \( \lambda_j \) are eigenvalues of matrix \( U \) (see Appendix).

5. Conclusions

Precise evaluation of the coagulant effectiveness characteristics for a recovered AS-based product obtained from metallurgical slag is of high importance when a comparison is made vs. a standard synthetic coagulant effectiveness. The present paper uses an intensive measure of efficiency in terms of removed phosphorous from wastewaters relative to the used coagulant dose. The experimental results covering a wide range of tested municipal wastewater and AS-based coagulant products from various metallurgical slag proved comparable performances.
As another conclusion, experimental data reveal that the removed mass of phosphorous from wastewater divided by the coagulant dose (mg P/mg AS-product dose) is decreasing with the used coagulant dose. However, in absolute terms, the mass of removed phosphorous (MRP) is increasing with the applied dose until a maximum is reached (the optimal dose), higher than which application of larger coagulant doses lead to a negligible increase in the remode P.

The derived nonlinear correlation model of MRP as function of used coagulant dose is proved as being a very useful tool in predicting what is the optimum coagulant dose to be employed for a new treated wastewater when only the initial load with phosphorous is know.

Even if the removed phosphorous from wastewaters was the only water parameter used to assess the AS-based coagulant efficiency, the described procedure present enough generality, being suitable to be applied for a different water quality parameter such a CCO-Cr, or suspended solids.

**Appendix**

For a tested linear or nonlinear correlation model, the parameter estimation with a suitable statistical estimator [13] should be completed with a model adequacy and parameter significance analysis. In the cases with \( r \) observations (observed variables \( y_i \)), dependent of the independent variable \( x \), the noise level \( (\sigma) \) is assumed to be constant for all the \( n \) experimental points, leading to the use of the linear or nonlinear least squares estimator to evaluate the \( p \) parameters \( k \) with a standard least square objective function [12, 13].

\[
Min_k f(k) = \sum_{u=1}^{n} [\hat{y}_i(x_u,k) - y_i(x_u)]^2; k > 0
\]

(A1)

Some supplementary max/min constraints might be imposed to the parameters from physical meaning reasons. The global model adequacy was tested with the \( \chi^2 \) statistical test. If the inequality:

\[
\frac{s^2}{\sigma^2} = \frac{\|\{(\hat{y}(\hat{k}) - y)\|_2^2/(nr - p)}{\sigma^2} < \chi^2(nr - p;0.95)
\]

(A2)

hold, then the model is adequate with 95% probability. The adequacy is completed with the residuals \( (\hat{y}_{iu} - y_{iu}) \), \( i = 1, \ldots, r; u = 1, \ldots, n \) plots in various variants: \( (\hat{y}_{iu} - y_{iu}) \) vs. \( x_u \); \( \hat{y}_{iu} \) vs. \( y_{iu} \); \( (\hat{y}_{iu} - y_{iu}) \) vs. \( y_{iu} \). Such plots can reveal deviations from the constant noise hypothesis, presence of ‘outliers’ in the error distribution of variables, quality of the model adequacy, systematic (±)residuals and the order of magnitude of the residuals compared with the
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observations. The estimated parameter significance was checked based on the following matrices (numerically evaluated, [13]):

\[
V(\hat{k})^{-1}_{[p,p]} = \frac{n}{\sum_{i=1}^{p} \sum_{j=1}^{p} \frac{1}{\sigma_{ii}^{2}} \left[ \frac{\partial y_{iu}}{\partial k} \right]_{[p,1]} \left[ \frac{\partial y_{iu}}{\partial k} \right]_{[1,p]}}
\]

(A3)

the estimate variance-covariance matrix [14];

\[
U(\hat{k})_{[p,p]} = \frac{n}{\sum_{i=1}^{r} \sum_{j=1}^{p} \left[ \frac{\partial y_{iu}}{\partial k} \right]_{[p,1]} \left[ \frac{\partial y_{iu}}{\partial k} \right]_{[1,p]}} + \sigma^2 I; \quad \bar{\sigma} = \text{Min}(\sigma_{ii}^2)
\]

(A4)

\[
R(\hat{k})_{[p,p]}; R_{ij} = \frac{[V(\hat{k})]_{ij}}{\sqrt{[V(\hat{k})]_{ii}[V(\hat{k})]_{jj}}} \in [-1,1]
\]

(A5)

the parameter inter-correlation matrix.

An estimated parameter \( k_j \) is considered significant in the model (with a probability of 95%), if the Student test is fulfilled:

\[
t_j = \left| \frac{\hat{k}_j}{\sqrt{[V(\hat{k})]_{jj}}} \right| > t(nr - p;97.5%)
\]

(A6)

together with the ‘ridge selection’ test:

\[
\lambda_j / \bar{\sigma}^2 > 1 - 3
\]

(A7)

where \( \lambda_j \) are eigenvalues of matrix \( U [14] \):

The less estimable parameters, because of insufficient data or degeneracy in the data-model form, correspond to high inter-correlation coefficients (higher in module than 0.95). Those parameters also present large confidence intervals [13]:

\[
k_j = \hat{k}_j \pm \sqrt{[V(\hat{k})]_{jj}} t(nr - p;97.5%); j = 1, \ldots, p
\]

(A8)

Acknowledgment

First author is grateful to Prof. Dr. Gheorghe Maria from University Politehnica of Bucharest, Department of chemical & Biochemical Engineering for his priceless help in the statistical treatment of experimental data.
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