NERA – Null-Emission Rohwasserproduktion in der Automobilindustrie

Electrochemical wastewater treatment: Matrix effect analysis

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Introduction

- Electrochemical wastewater treatment can be an effective tool in heavy metal removal in the automotive industry wastewater and recovery of the resources.
- The presence of heavy metal (Zn, Mn, Ni), phosphate and other compounds(Ca^{2+}, Mg^{2+} and Organic compounds); influence directly in the treatment time, either independently or interacting in conjunction with one another.
- Understanding the factors, and their statistical significancy, affecting the treatment efficiency.
- We could approximate the interaction of the variables by using statistical tools such as Analysis of variance(ANOVA), principal component analysis(PCA) and response surface method(RSM).

Methodology

ANOVA

- Assesses the statistical singificancy of each of the variables on the time of wastewater treatment (p-value).
- Null and Alternative hypothesis analysis.
- Residuals graphical analysis and model fit.

RSM

- Explores the relationships between the multiple dependent variables and independent variables.
- The RSM model is designed to assess the combined effects of different factors in the wastewater treatment time..

Experimental Design

- A set of 50 experiments were controlled, random order and in the same conditions.
- The experiments were conducted in an electrochemical flow cell, using a Platinum electrode as anode and a bipolar plate (developed by Eisenhuth GmbH) in separated chambers. The available electrode surface area was 3.14 cm².
- Chronopotentiometric measurements took place at 25 mA/cm² using a Gamry® Refence 3000 Potentionstat.
- The samples were prepared with varying concentrations of heavy metals, phosphate ions, Ca^{2+} and Mg^{2+} ions. Using as background electrolyte 0.5M Na_2SO_4 to remove high deviations in conductivity.
- The pH of the samples were controlled, and the end of the experiment was set at pH 11.
- The independent variables defined for this dataset were:
  - Heavy metal content (as Zn^{2+});
  - Phosphate content (as PO_4^{3-});
  - Water hardness (as Ca^{2+} and Mg^{2+});
  - Initial pH

Data Analysis and Discussion

ANOVA

- H_0: The concentration (and variation thereof) of each individual variable does not significantly affect the treatment time.
- H_1: The concentration of each individual variable significantly affects the treatment time.

Variable	Df	F-value	P-value	Significance
Heavy metal content	1	362.601	< 2E-16	p < 0.001
Phosphate content	1	10.162	0.00261	0.001 < p < 0.01
Water hardness	1	34.512	4.79E-07	p < 0.001
Initial pH	1	0.015	0.90272	p > 0.05
Residuals	45			

Table 1: ANOVA results showing the effect of heavy metal content, phosphate content, water hardness, and initial pH on treatment time.

Data Analysis and Discussion

- Heavy metal content has shown the most statistical significance, followed by the presence of Ca^{2+} and Mg^{2+}, and the presence of phosphate. Initial pH has little statistical significancy on the treatment time.

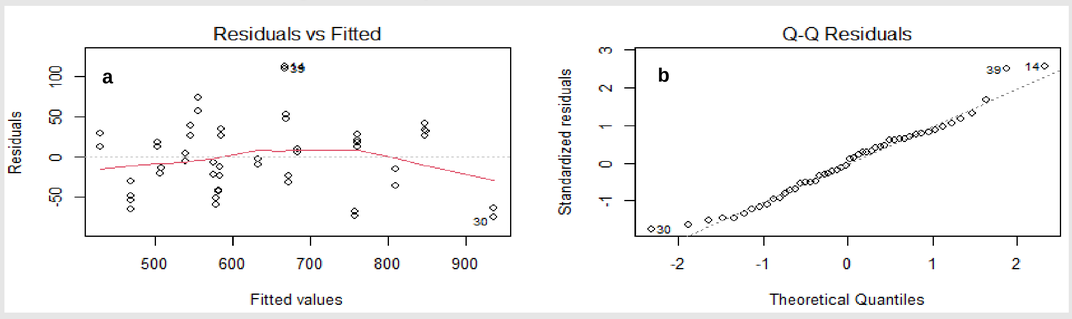

Figure 1: a) The plot shows the relationship between the residuals and the predicted values. b) Comparison of the quantiles of the residuals to the quantiles of a normal distribution.

- The residuals plots above proves that the model indicates a normal distribution (Q-Q Residuals plot) and there is no clear pattern of non-linearity and heteroscedasticity (Residuals vs Fitted) indicating that the model represents well the relationship between the independent variables and the treatment time.

Response Surface Method

- RSM modelling reaffirmed the results of the ANOVA model, that the Heavy metal content has the highest statistical significancy of the dataset, with a second order p-value of 0.02953.
- The model fit for this method has an Adjusted R^2 of 0.9348, indicating that this model explains about 93% of the variability, which while not perfect, is still a strong fit.

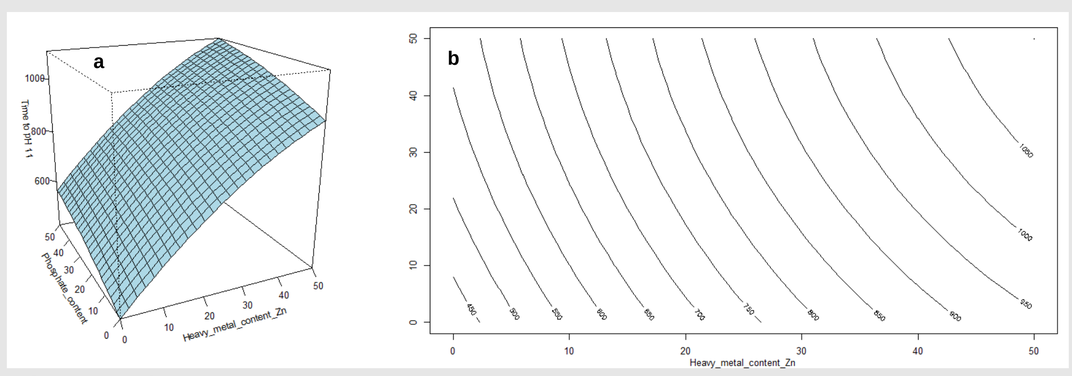

Figure 2: a) Response surface plot showing the interaction between in heavy metal content and phosphate content. b) contour plot illustrate the same interaction in a 2D representation

Conclusion

- In what pertains to the variables discussed, the heavy metal content in the wastewater will have the highest impact on the treatment time.
- The ANalysis Of Variance indicates that the alternative hypothesis is true.
- RSM model shows that heavy metal and phosphate content are the most influential factors.

Next steps

- Larger dataset and increased numbers of variables.
- How does the model compare to real wastewater treatment data.
- Predictive models and the reliability for treatment time

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