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Statistical Modeling of NaCl and $FeSO_4$ Pretreatment Effect on Refractory Copper Ore Leaching

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Abstract: Black copper oxides, a significant copper resource, present challenges in leaching due to their refractory nature and complex mineralogical composition. This study investigates the sulfation dynamics of the reductive leaching process of black copper ores with the purpose of increasing the copper leaching, focusing on the influences of time and the addition of NaCl and $FeSO_4$ on sulfation behavior. Experiments were designed to replicate industrial conditions using oxidized minerals from the Codelco Salvador hydrometallurgy plant. Multivariate nonlinear regression models and response surface methodology were employed to analyze sulfation behavior. The findings demonstrate that analytical acid consumption (AAC) exerts a consistently positive and statistically significant effect on sulfation across the sampled domain, while NaCl and $FeSO_4$ also influence the process. However, variations in their levels showed limited impact. Time was significant only within the 24–48 h range. The optimized model predicted maximum sulfation at 60 h with 60% AAC, 90 g NaCl, and 42 g $FeSO_4$, with strong alignment between the observed and predicted values. These insights emphasize the importance of pretreatment methods, including sulfuric acid curing and NaCl addition, in improving leaching efficiency.

Keywords: black copper; statistical modeling; refractory ore; response surface methodology

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1. Introduction

In certain regions of the world, special copper deposits, known as exotic, exist. These deposits are distinct due to their formation and the composition of their mineralogical species. For instance, porphyry copper deposits undergo oxidation when exposed to atmospheric oxygen and water, forming an oxidation zone. This zone is characterized by the oxidation of hypogene sulfide minerals and the formation of secondary mineral assemblages, which can cause acid rock drainage. The formation of this zone is influenced by various factors, including the mineralogy of the hypogene sulfides, the neutralization potential of gangue minerals, and the presence of an unsaturated zone, which is affected by tectonics, climate, erosion, and the incision of the hydrographic network [1,2]. During the supergene processes, the leachate solution contains elements such as Cu, Mn, and K in solution and can be transported over long distances. These elements then reprecipitate

further down in the supergene profile, where the conditions are reducing. In the Atacama Desert, Cu is reprecipitated in the oxide zone through carbonates, chlorides, sulfates, oxides, and copper [3,4]. Exotic copper deposits found in Arizona, New Mexico, and Sonora are metal deposits associated with porphyry Cu deposits. These deposits are usually zoned from ferricrete upgradient and extend into the bedrock leached cap. Moving downgradient, they are seen as black manganese oxides or Cu wad and are eventually found as chrysocolla in the Cu-rich systems [5,6]. The exotic copper deposits exhibit a wide range of size, with some reaching up to 3.5 million tons of copper. Notable examples of these deposits in northern Chile include Radomiro Tomic, El Tesoro, Spence, Mina Sur, and Lomas Bayas [6].

Researchers have made numerous efforts to categorize black copper oxides, but these have yielded inconsistencies. Before early 1988, copper pitch and copper wad were the only recognized minerals of this type. Pincheira et al. proposed the term "black copper silicate" to refer to both minerals, since they share a similar composition and lack a defined crystalline structure [7]. In the copper mining industry, exotic deposits containing minerals refractory to traditional leaching agents, such as sulfuric acid, are commonly referred to as black copper oxides or black coppers. These oxidized ores consist of copper minerals and mineraloids exhibiting green and black hues, which contain significant levels of manganese. The exotic ores include atacamite, chrysocolla copper wad, copper pitch, and neotocite [8–10].

It is crucial to emphasize the scarcity of information in the literature regarding the leaching of oxidized minerals containing black copper oxides, despite the significant industrial value of these deposits. This underscores the novelty and potential impact of the proposed investigation, based on the pioneering studies conducted by Contreras and Torres [11,12]. From Contreras, three of the five leaching media used have been selected, i.e., acid, chloride, and acid-reducing, which have shown great potential for the extraction of copper in mixed Cu-Mn-Fe compounds. From the manuscript by Torres et al., the methodology focused on ore pretreatment has been adopted to reduce the redox potential of the leaching solution. It is essential to recognize that not all manganese-containing species are challenging to leach. For manganese carbonate ores, a combination of sulfuric acid and chloride ions effectively dissolves all the manganese present in the ore [13].

Among the species that are most studied for the leaching of black copper are those that contain manganese. Literature reports frequently discuss the use of reducing agents to enhance the dissolution of manganese from the ores [14]. Several studies have been conducted to dissolve manganese-bearing ores, mainly through pyrometallurgical, hydrometallurgical, and biohydrometallurgical routes [14,15]. For instance, ferrous sulfate, sulfur dioxide, and sulfite solutions can serve as effective reducing agents [16]. The leaching of manganese ores using organic reducing agents has also been tested. It has been determined that oxalic acid, when utilized at elevated temperatures within an acidic medium, can effectively dissolve a significant portion (up to 98%) of the manganese present in the minerals [17,18]. Benavente et al. emphasized the importance of manganese-containing species. They noted that these species have a non-crystalline structure and a variable composition. This composition mainly includes copper, manganese, iron, aluminum, and silicon. These traits enhance their resistance to dissolution. Similar characteristics can be found in mineral samples, such as marine polymetallic nodules and manganese ores [19–21].

Concerning the wide variety of mineral species present in ores containing black oxides, Contreras proposed the following dissolution reactions [12].

Tenorite (CuO) demonstrates leachability in acidic solutions according to reaction (1), with an equilibrium pH of around 4.5. Dissolution can be accelerated by using hydrochloric acid or increasing the temperature.

$$CuO_{(s)} + H_2SO_{4(aq)} \rightarrow CuSO_{4(aq)} + H_2O_{(l)} \quad (1)$$

Hematite (Fe_2O_3), a mineral, exhibits insolubility in water and virtual insolubility in acidified and cyanide solutions, necessitating a more energetic acid, such as hydrochloric acid, for dissolution. Reaction (2) demonstrated that the reaction involving hematite manifests negative free energy, representing its spontaneous nature. Nevertheless, practical application reveals that the kinetics of this reaction are notably slow.

$$Fe_2O_{3(s)} + 6H^+_{(aq)} \rightarrow 2Fe^{+3}_{(aq)} + 3H_2O_{(l))} \quad (2)$$

Manganic oxide (Mn_2O_3) is insoluble in water, so it requires a reducing agent for complete dissolution in diluted sulfuric acid. Adding a suitable reducing agent, such as Fe^{+2} (reaction (3)), can significantly improve this process.

$$\begin{gathered} Mn_2O_{3(s)} + 2H^+_{(aq)} \rightarrow Mn^{+2}_{(aq)} + MnO_{2(s)} + H_2O_{(l)} \\ MnO_2 + 2Fe^{+2}_{(aq)} + 4H^+_{(aq)} \rightarrow Mn^{+2}_{(aq)} + 2Fe^{+3}_{(aq)} + 2H_2O_{(l)} \\ Mn_2O_{3(s)} + 2Fe^{+2}_{(aq)} + 6H^+_{(aq)} \rightarrow 2Mn^{+2}_{(aq)} + 2Fe^{+3}_{(aq)} + 3H_2O_{(l)} \end{gathered} \quad (3)$$

Manganous oxide (MnO) is a compound known for its easy solubility in most acids (reaction (4)).

$$MnO_{(s)} + 2H^+_{(aq)} \rightarrow Mn^{+2}_{(aq)} + H_2O_{(l)} \quad (4)$$

Cupric ferrite ($CuFe_2O_4$) exhibits high resistance to acid solutions at room temperature under typical leaching conditions. However, enhanced dissolution of this compound can be achieved by elevating the temperature, increasing the acid concentration, or varying the type of acid used, such as by employing hydrochloric acid (HCl). The chemical reaction depicting the dissolution of cupric ferrite is provided below (reaction (5)).

$$CuFe_2O_{4(s)} + 8H^+_{(aq)} \rightarrow Cu^{+2}_{(aq)} + 2Fe^{+3}_{(aq)} + 4H_2O_{(l)} \quad (5)$$

Copper manganite ($CuMn_2O_4$) requires an acidic medium for the leaching reaction. Furthermore, the facilitation of dissolution and kinetics requires the presence of a reducing agent, such as a ferrous ion (Fe^{2+}).

$$CuMn_2O_{4(s)} + 8H^+_{(aq)} + 2Fe^{+2}_{(aq)} \rightarrow Cu^{+2}_{(aq)} + 2Fe^{+3}_{(aq)} + 2Mn^{+2}_{(aq)} + 4H_2O_{(l)} \quad (6)$$

The pretreatment of ores is crucial for enhancing the solubility of mineral species. This process primarily involves the addition of concentrated sulfuric acid, a method commonly called "curing" in an industrial context. Furthermore, sodium chloride or nitrate ions have been used to pretreat refractory copper ores such as chalcopyrite [22,23]. Torres et al. have demonstrated that curing is essential for enhancing the leaching of ores containing black copper. The manuscript suggests prolonged pretreatment that involves the use of sulfuric acid and the addition of sodium chloride. The researchers conclude that the impact of sodium chloride is primarily significant for the dissolution of manganese [11].

This research used oxidized minerals from the Codelco Salvador hydrometallurgy plant, particularly from the "Damiana" mine sector. The primary goal of this study was to replicate essential industrial conditions and refine the pretreatment process to enhance the leaching of oxidized ores containing black copper oxides. Furthermore, we will explore the synergistic effects of NaCl and $FeSO_4$ on the copper sulfation through statistical modeling.

The significance of this research is anchored in its contribution to the existing body of knowledge, mainly due to the limited availability of studies within the literature.

2. Materials and Methods

2.1. Ore Sample

Oxidized copper ore from a heap leaching operation located in Copiapó, Chile, was used in this study. The sample was received directly from tertiary crusher discharge. The P80 value was 7632 µm. The elemental composition of the ore was determined by atomic spectrometry (SpectrAA 220, Varian, Palo Alto, CA, USA). The chemical composition shows 0.76% total copper, 0.67% soluble copper, 0.46% manganese, 0.1% magnesium, 0.62% calcium, 0.21% aluminum, and 5.37% iron.

X-ray diffraction using a Bruker D8 Advance X-ray diffractometer (XRD; Bruker, Billerica, MA, USA) determined the primary mineralogical composition of the ore samples, which include chrysocolla (PDF card no. 00-003-0219), malachite (PDF card no. 00-002-0345), azurite (PDF card no. 01-070-1579), atacamite (PDF card no. 01-078-0372), brochantite (PDF card no. 01-087-0454), chalcocite (PDF card no. 01-083-1462), chalcopyrite (PDF card no 01-074-1737), and bornite (PDF card no 00-014-0323).

2.2. Leaching Column Tests

The ore samples underwent agglomeration and were subsequently loaded into cylindrical columns constructed from HDPE, measuring 1 m in height and 315 mm in diameter. The pretreatment stage was then implemented, during which water and acid were added, based on the results obtained during the previous phase. For samples that included NaCl and $FeSO_4$, the reagents were introduced before adding water and acid to accurately simulate the industrial process, specifically, the mixing on a conveyor belt before entering the agglomerating drum. Upon completion of the pretreatment stage, the resulting agglomerates were placed into the columns. The irrigation of the ore within these columns was carried out using peristaltic pumps. The leaching columns were irrigated for 70 days at an average irrigation rate of 6 L/hm^2. Leaching column tests were executed at room temperature, approximately 20 °C. All column leaching tests were performed in duplicate, and a standard deviation of ±2% was obtained for all the tests.

2.3. Statistical Modeling

The study investigated how various independent variables affect leaching kinetics, including time, acid consumption, and the addition of sodium chloride (NaCl) and iron sulfate ($FeSO_4$). This was achieved through the application of response surface methodology (RSM), a statistical technique that helps to determine the relationships between multiple factors and their collective impact on the leaching process [24].

The compound central face design (CCF) and a nonlinear polynomial regression model were applied in the experimental design to study Cu dissolution. The sulfation test procedure was executed according to the following guidelines for each respective test:

- Sample mass: 3.0 kg;
- Water: 0.3 L;
- Washed water: 6.1 L.

Developing reliable and efficient methods for creating models to represent the dynamics of complex processes, such as leaching from laboratory data, is critically important in research. In this context, response surface methodology (RSM) has been developed as an effective instrument for researchers in various fields. RSM provides a robust solution characterized by minimal fitting time and low computational demands, positioning it as an excellent option for modeling and enhancing our understanding of dynamic processes,

while also enabling accurate predictions of laboratory data. Through the application of RSM, researchers can efficiently attain their desired outcomes, thereby empowering them to make confident and well-informed decisions [25,26].

RSM encompasses a set of statistical methodologies utilized to model and analyze scenarios in which multiple independent or explanatory variables exert influence on a response variable. These techniques primarily aim to design experiments that yield values for the response variable and identify the mathematical model that best fits the collected data [27]. Ultimately, the goal is to determine the factor values that optimize the system's operating conditions [28]. The distinction between RSM and traditional experimental design lies in their objectives. Experimental design is primarily concerned with identifying the most effective combination or sample from those that have been tested. In contrast, RSM aims to determine the optimal operating conditions of a process throughout the range of sampled parameters, specifically within the domain of the independent variables [29].

The methodology involved conducting pretreatment experiments that examined four factors (Table 1), resulting in a total of 240 experimental trials (Table 2). The aim was to study the effects of time, acid consumption, and the addition of NaCl, and $FeSO_4$ on the leaching. Minitab 18 software was utilized for modeling and experimental design, enabling the investigation of linear effects and interactions. The experimental data were analyzed using multiple regression analysis, focusing on factors that significantly explain the variability of the model and demonstrate high statistical significance.

Table 1. Levels of the explanatory variables of the design of the experiments.

Variable	Unit	Notation	Levels
Time	Hours	x_1	{24, 48, 72, 96, 120}
AAC	%	x_2	{40, 50, 60}
NaCl	g	x_3	{0, 30, 60, 90}
$FeSO_4$	g	x_4	{0, 14, 28, 42}

Table 2. Sulfation results of the experimental design.

Exp.	x_1	x_2	x_3	x_4	Sulf.	Exp.	x_1	x_2	x_3	x_4	Sulf.	Exp.	x_1	x_2	x_3	x_4	Sulf.
1	24	60	91	28	24	81	48	60	0	0	17	161	96	50	91	28	21
2	24	60	91	42	23	82	48	40	61	28	17	162	96	40	91	42	21
3	24	50	91	42	19	83	48	50	0	0	16	163	96	50	91	42	21
4	24	60	91	0	18	84	48	40	30	0	16	164	96	60	30	14	19
5	24	60	61	14	18	85	48	60	0	14	16	165	96	60	30	28	19
6	24	60	30	28	16	86	48	40	0	42	16	166	96	50	60	28	19
7	24	60	60	42	16	87	48	40	30	14	16	167	96	60	60	28	19
8	24	60	61	0	15	88	48	40	61	14	16	168	96	40	90	14	19
9	24	60	30	14	15	89	48	60	0	28	15	169	96	40	61	0	18
10	24	50	61	14	15	90	48	40	0	0	14	170	96	40	91	0	18
11	24	60	61	28	15	91	48	40	60	42	14	171	96	50	91	0	18
12	24	60	30	0	14	92	48	50	0	28	12	172	96	50	0	14	18
13	24	60	0	14	14	93	48	40	61	0	11	173	96	40	30	28	18
14	24	60	0	0	13	94	48	50	0	14	10	174	96	60	60	14	18
15	24	60	0	42	13	95	48	40	0	14	9	175	96	40	61	42	17
16	24	40	60	14	13	96	48	40	0	28	7	176	96	50	30	28	16
17	24	50	60	28	13	97	72	60	91	28	30	177	96	50	30	42	16
18	24	50	61	42	13	98	72	60	30	0	29	178	96	40	61	14	16
19	24	50	61	0	12	99	72	60	30	14	29	179	96	40	61	28	16
20	24	50	91	0	12	100	72	50	91	28	29	180	96	50	0	0	15

Table 2. *Cont.*

Exp.	x_1	x_2	x_3	x_4	Sulf.	Exp.	x_1	x_2	x_3	x_4	Sulf.	Exp.	x_1	x_2	x_3	x_4	Sulf.
21	24	50	0	0	11	101	72	60	61	42	27	181	96	50	0	28	15
22	24	40	91	0	11	102	72	60	0	42	26	182	96	60	0	28	15
23	24	50	0	14	11	103	72	60	61	28	26	183	96	60	0	42	15
24	24	60	0	28	11	104	72	60	0	0	25	184	96	40	30	14	15
25	24	50	0	42	11	105	72	60	30	28	25	185	96	50	30	14	15
26	24	50	30	42	11	106	72	60	30	42	25	186	96	50	61	14	15
27	24	60	30	42	11	107	72	60	0	14	24	187	96	40	0	28	13
28	24	50	91	14	11	108	72	60	61	14	24	188	96	40	30	42	13
29	24	60	91	14	11	109	72	40	90	28	24	189	96	50	0	42	12
30	24	50	30	0	10	110	72	60	91	42	23	190	96	40	0	0	11
31	24	50	0	28	10	111	72	50	30	14	22	191	96	40	0	14	11
32	24	50	30	14	10	112	72	40	30	28	22	192	96	40	0	42	11
33	24	40	30	42	10	113	72	50	30	28	22	193	120	60	91	42	31
34	24	50	91	28	10	114	72	50	30	42	22	194	120	60	0	42	28
35	24	40	0	0	9	115	72	50	60	42	22	195	120	50	91	42	27
36	24	40	30	0	9	116	72	50	91	42	22	196	120	60	61	28	26
37	24	40	30	14	9	117	72	60	61	0	21	197	120	60	91	0	25
38	24	40	61	28	9	118	72	40	30	14	21	198	120	50	61	28	25
39	24	40	61	42	9	119	72	60	91	14	21	199	120	60	30	0	23
40	24	40	91	42	9	120	72	40	91	42	21	200	120	50	91	0	22
41	24	40	60	0	8	121	72	40	30	0	20	201	120	60	0	14	22
42	24	40	0	14	8	122	72	50	30	0	20	202	120	60	0	28	22
43	24	40	0	42	7	123	72	50	60	28	20	203	120	60	30	14	22
44	24	40	0	28	6	124	72	50	91	0	19	204	120	60	30	28	22
45	24	50	30	28	6	125	72	60	91	0	19	205	120	60	30	42	22
46	24	40	91	14	6	126	72	50	0	14	19	206	120	50	31	0	21
47	24	40	91	28	5	127	72	40	61	42	19	207	120	50	0	42	21
48	24	40	30	28	4	128	72	50	61	14	18	208	120	50	61	42	21
49	48	60	61	28	29	129	72	50	91	14	18	209	120	60	61	42	21
50	48	60	91	0	28	130	72	40	91	0	17	210	120	60	0	0	20
51	48	60	60	0	26	131	72	50	0	28	17	211	120	50	61	0	20
52	48	50	91	0	24	132	72	60	0	28	17	212	120	60	60	0	20
53	48	60	91	28	24	133	72	50	61	0	16	213	120	50	0	28	20
54	48	50	61	0	23	134	72	50	0	42	16	214	120	50	30	28	20
55	48	60	30	14	23	135	72	40	60	14	16	215	120	40	61	28	20
56	48	60	30	42	23	136	72	40	61	28	15	216	120	50	91	28	20
57	48	50	61	42	23	137	72	50	0	0	14	217	120	60	91	28	20
58	48	60	60	42	23	138	72	40	0	14	14	218	120	40	92	0	18
59	48	60	91	42	23	139	72	40	91	14	14	219	120	40	31	28	18
60	48	50	30	28	22	140	72	40	60	0	13	220	120	50	30	42	18
61	48	60	30	28	22	141	72	40	0	28	12	221	120	60	60	14	18
62	48	50	30	42	22	142	72	40	30	42	12	222	120	60	91	14	18
63	48	50	61	28	22	143	72	40	0	42	11	223	120	40	92	28	18
64	48	50	91	28	22	144	72	40	0	0	10	224	120	40	61	0	17
65	48	50	91	42	22	145	96	60	30	0	28	225	120	50	0	14	17
66	48	50	30	0	21	146	96	60	91	28	27	226	120	50	30	14	17
67	48	60	30	0	21	147	96	60	91	42	27	227	120	40	31	42	16
68	48	40	30	42	21	148	96	60	91	0	26	228	120	40	61	14	16
69	48	40	91	0	20	149	96	60	90	14	25	229	120	50	61	14	16
70	48	60	0	42	20	150	96	60	30	42	24	230	120	40	91	14	16
71	48	50	61	14	20	151	96	50	30	0	23	231	120	50	91	14	16
72	48	60	61	14	20	152	96	60	61	42	23	232	120	40	91	42	16
73	48	40	91	42	20	153	96	40	30	0	22	233	120	40	0	28	14
74	48	50	0	42	19	154	96	50	61	42	22	234	120	40	61	42	14
75	48	50	30	14	19	155	96	60	0	0	21	235	120	50	0	0	13

Table 2. *Cont.*

Exp.	x_1	x_2	x_3	x_4	Sulf.	Exp.	x_1	x_2	x_3	x_4	Sulf.	Exp.	x_1	x_2	x_3	x_4	Sulf.
76	48	40	91	14	19	156	96	50	60	0	21	236	120	40	0	0	12
77	48	50	91	14	19	157	96	60	61	0	21	237	120	40	30	0	12
78	48	60	91	14	19	158	96	60	0	14	21	238	120	40	0	14	12
79	48	40	91	28	19	159	96	50	91	14	21	239	120	40	30	14	12
80	48	40	30	28	18	160	96	40	90	28	21	240	120	40	0	42	10

The general form of the experimental model is given by the following Equation (7):

$$Y = f(x_1, \ldots, x_n) = b_0 + \sum_{i=1}^{n} b_i x_i + \sum_{i=1}^{n} \sum_{j=1}^{n} b_{ij} x_i x_j + \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{k=1}^{n} b_{ijk} x_i x_j x_k \quad (7)$$

In this context, the variable xi represents the independent variables, while the parameters b denote the coefficients associated with those independent variables. The R^2 statistic, along with the *p*-values, are essential in evaluating the adequacy of the developed model for describing the process of nitration based on the sampled values. The R^2 coefficient quantifies the proportion of the total variability in the dependent variable relative to the mean accounted for by the regression model. Concurrently, the *p*-values serve as indicators of statistical significance, revealing whether a statistically significant relationship exists between the response variable and the independent variables [30].

The initial model, fitted from sample data, was subsequently improved by optimization using the L-BFGS-B method from the SciPy library in Python [31]. The L-BFGS-B method, which stands for limited-memory Broyden–Fletcher–Goldfarb–Shanno with boundary constraints, is an unconstrained optimization algorithm used to find the minimum scalar functions of several variables. This method, implemented in the SciPy library [32], takes advantage of a constrained approximation of the Hessian matrix, which makes it especially efficient for large optimization problems. In addition, L-BFGS-B allows for the handling of boundary constraints on the variables, guaranteeing that the solution lies within a specific range. In summary, optimization with L-BFGS-B seeks to improve the model fit by finding the parameters that minimize the objective function, considering the possible boundary constraints set.

3. Results and Discussion

3.1. Exploratory Analysis

Upon conducting an analysis of the main effects (refer to Figure 1), it has been concluded that all factors included in the experimental design have a significant impact on the response variable. This finding suggests a directly proportional relationship between the independent variables and the response. Additionally, an inverse exponential trend in sulfation is observed as a function of time. In contrast, sulfation displays a linear and directly proportional trend relative to AAC and NaCl. Lastly, a slight, directly proportional linear trend is noted between the response variable and $FeSO_4$.

The contour plots in Figure 2 indicate a preliminary observation that sulfation increases at mean time levels (refer to Figure 2a–c) and at the maximum levels of the other independent variables sampled (refer to Figure 2d–f).

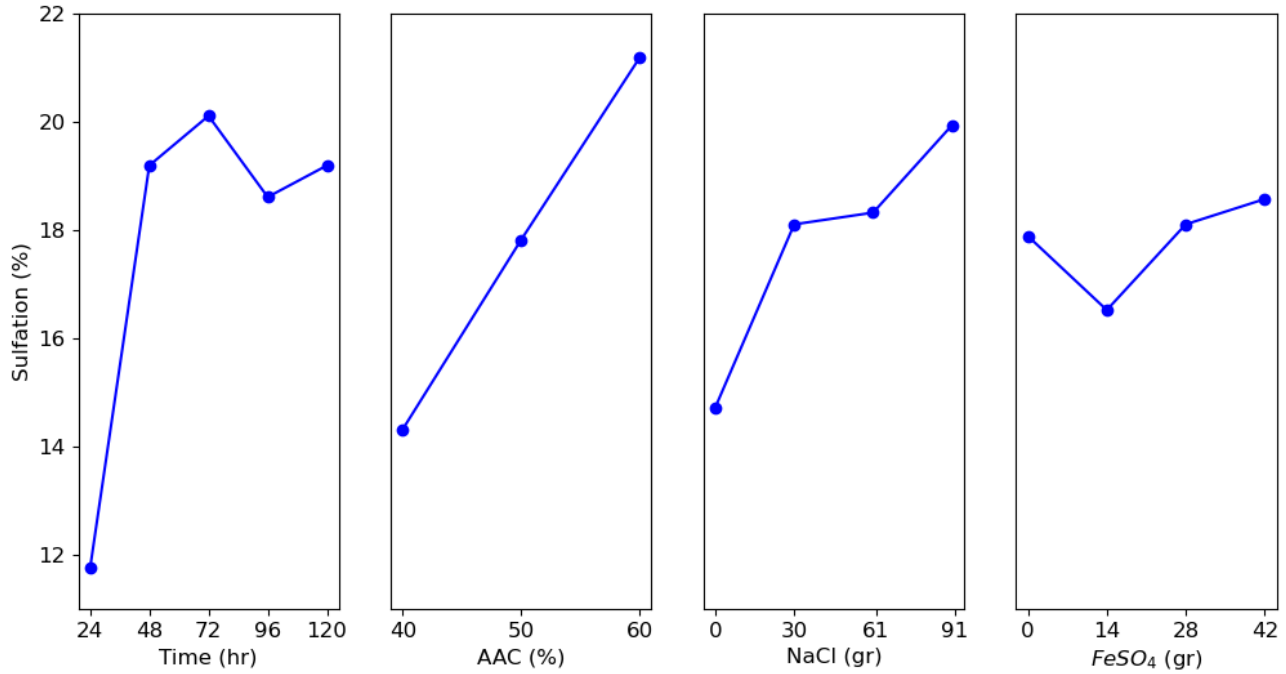


Figure 1. Main effects plots of sulfation (%) versus time (h); AAC (%); NaCl (g); and $FeSO_4$ (g).

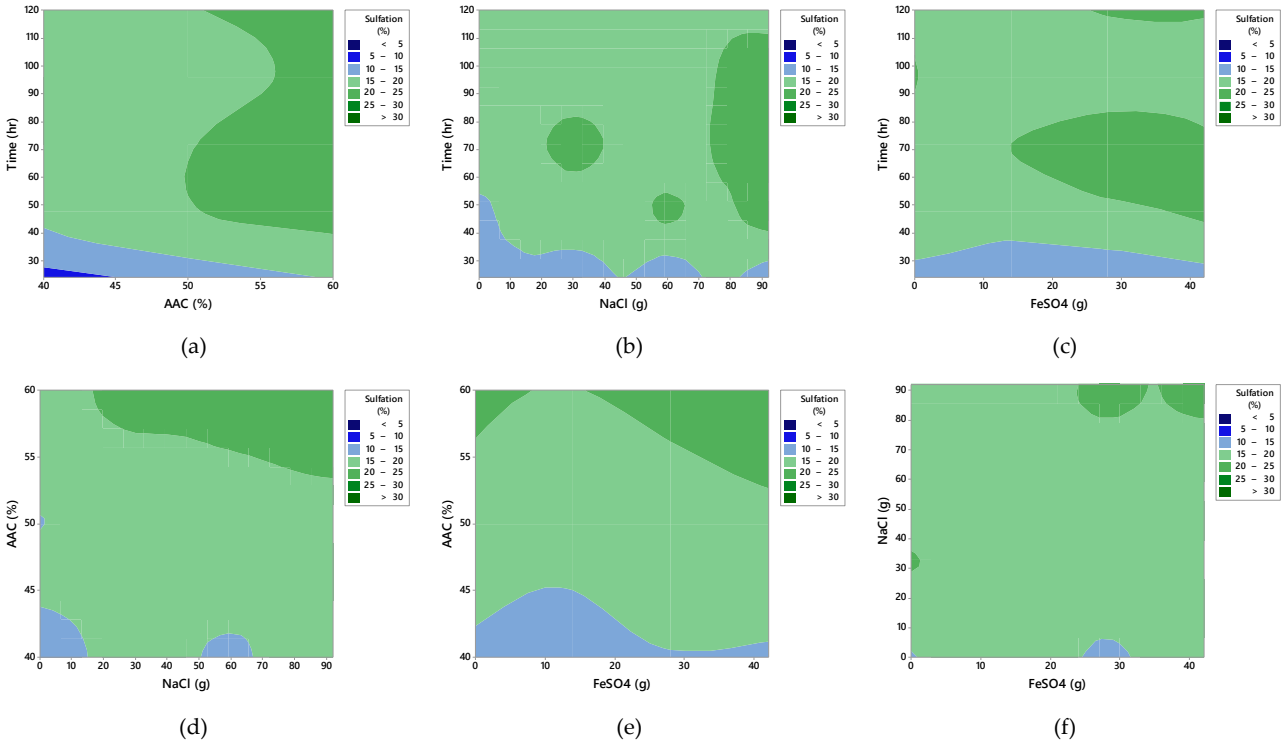


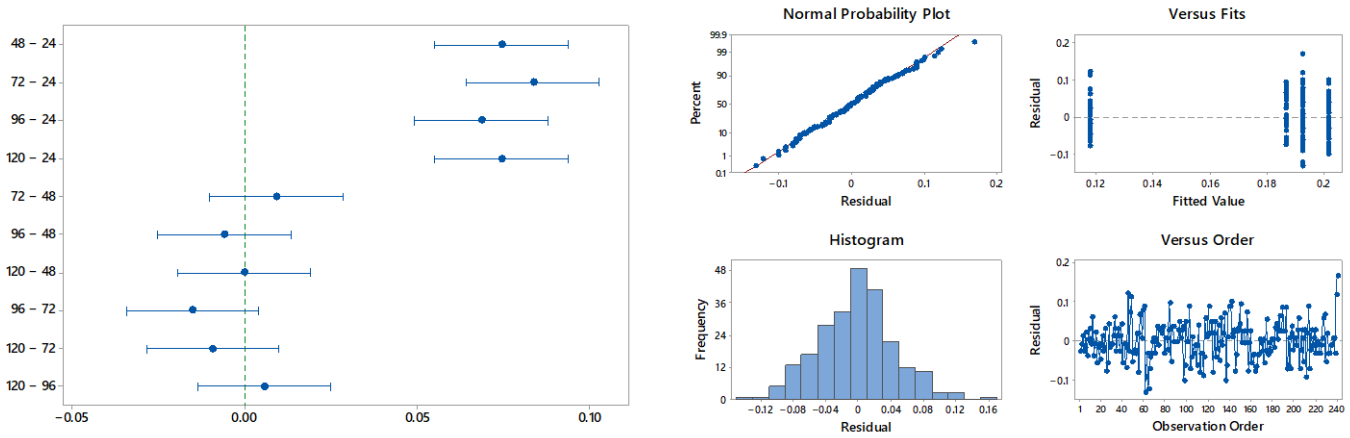
Figure 2. Percent sulfation as a function of time and AAC (**a**); time and NaCl (**b**); time and $FeSO_4$ (**c**); AAC and NaCl (**d**); AAC and $FeSO_4$ (**e**); and NaCl and $FeSO_4$ (**f**).

3.2. Analysis of the Impact of Each Factor on the Response

This report presents an analysis conducted using single-factor ANOVA to examine the relationship between a continuous variable and categorical factors (the levels of an independent variable). The primary objective is to determine whether there are significant differences among the population means of two or more groups.

The findings indicate that the *p*-value for the ANOVA, which assesses sulfation as a function of time, is less than 0.05. This result suggests that the responses across the various

levels studied differ significantly, confirming that at least some of the group means are not the same. In addition, the graph illustrating Fisher's simultaneous confidence intervals reveals that the confidence interval for the difference in means between the 24 h level and the 48, 72, 96, and 120 h levels does not cross zero (refer to Figure 3). This indicates that the differences in these means are statistically significant. Conversely, the confidence intervals for the other pairs of means do intersect with zero, suggesting that those differences are not statistically significant (Figure 3a). Moreover, the residual plot derived from the single-factor ANOVA (as presented in Figure 3b) indicates that the data distribution is not skewed and does not exhibit outliers. The *p*-value from the normality test of the residuals further confirms that the residuals follow a normal distribution.



(**a**) (**b**)

Figure 3. Individual confidence intervals for the differences in the means of the different levels of the time variable (**a**) and analysis of the model's residuals (**b**).

This analysis provides valuable insights into the impact of time on sulfation processes and identifies significant variations among the studied levels.

Similarly, the one-factor ANOVA for comparing the means of the response variable indicates that the means at each level for AAC are significantly different, i.e., none of the intervals of the differences include 0 (see Figure 4a), while the normality test is presented in Figure 4b.

The impact of variations in the NaCl level on the level of sulfation indicates that the level of sulfation is higher in the presence of sodium chloride (NaCl > 0) (see Figure 4c); however, no significant differences are observed at different NaCl levels (30, 61, 91). The analysis of residuals of the single-factor ANOVA for NaCl corroborates that these are normally distributed (see Figure 4d). Finally, the ANOVA for $FeSO_4$ indicates no differences between the different levels, so it is possible to conclude that there are no significant differences in the level of sulfation at different levels of this independent variable (see Figure 4e,f).

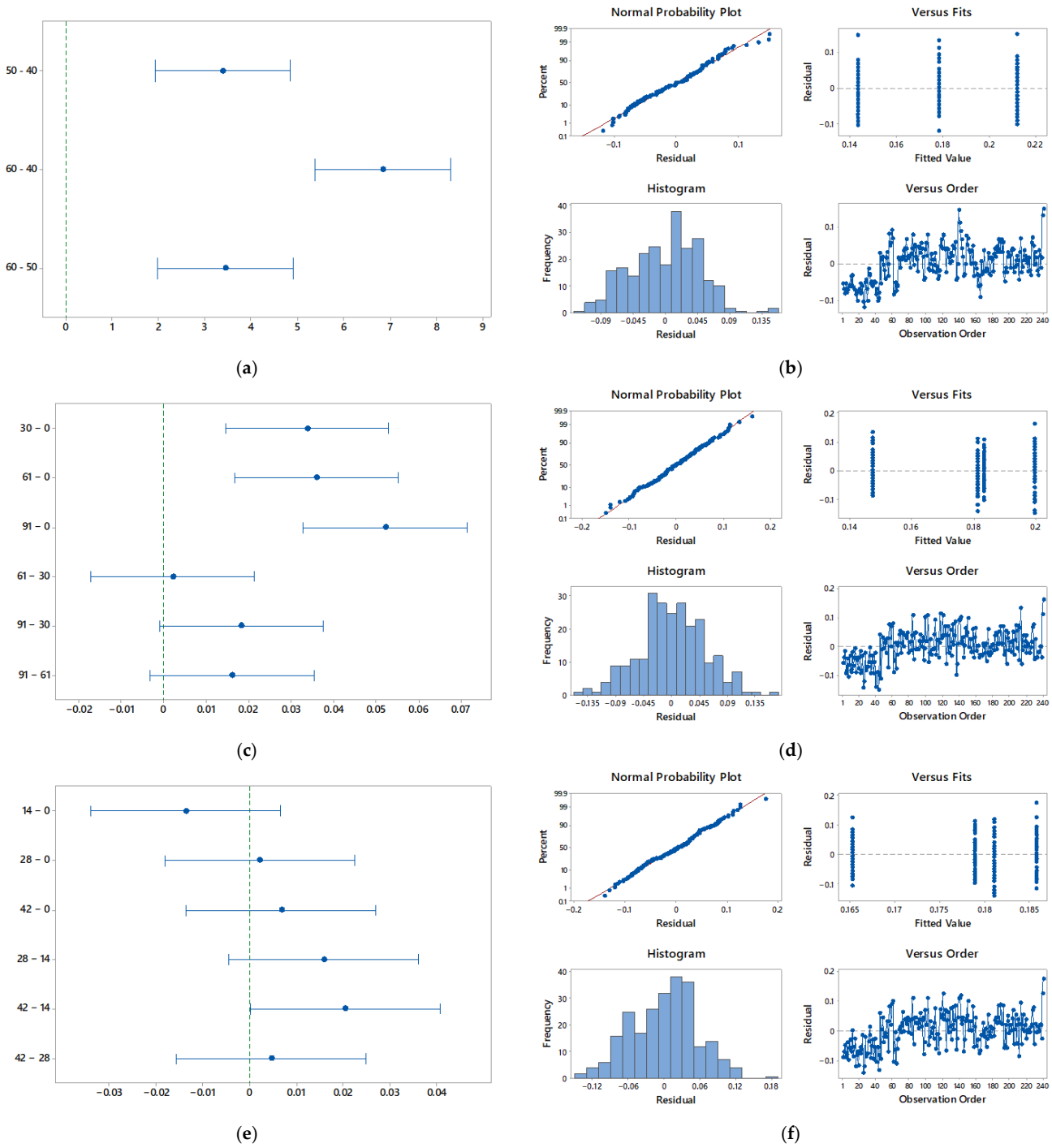


Figure 4. Individual confidence intervals for the differences in the means of the different levels and residuals plot of the models for the independent variables AAC (**a**,**b**); NaCl (**c**,**d**); and $FeSO_4$ (**e**,**f**).

3.3. Multiple Regression Modeling of Sulfation

The multiple regression model fitted from the experimental design is shown in Equation (8):

$$\begin{aligned} y = -17.368309 \quad & +1.028948x_1 + 0.214509x_3 - 0.013451x_1^2 + 0.00339x_2^2 - 0.005783x_3^2 + 0.002214x_1x_3 \\ & +0.000049x_1^3 + 0.000027x_3^3 - 0.000156x_4^3 + 0.000014x_1^2x_2 - 0.000045x_1x_2x_3 \\ & -0.000091x_2^2x_4 + 0.000028x_2x_3^2 + 0.000236x_2x_4^2 + 0.00001x_3^2x_4 \end{aligned} \quad (8)$$

ANOVA analysis indicates that the model fitted in Equation (8) adequately represents sulfation under the set of parameters sampled. The model requires no additional adjust-

ments and is validated by the goodness-of-fit statistics shown in Table 3, although the statistics, p-values ($p \leq 0.05$), and R^2 (72.72%) indicate that the model is statistically significant (see Tables 3 and 4). Nevertheless, enhancements in the model's fit may be attainable through the expansion of the sample size or the incorporation of additional variables that could impact the response. Furthermore, the F-test substantiates the statistical significance of the fitted model.

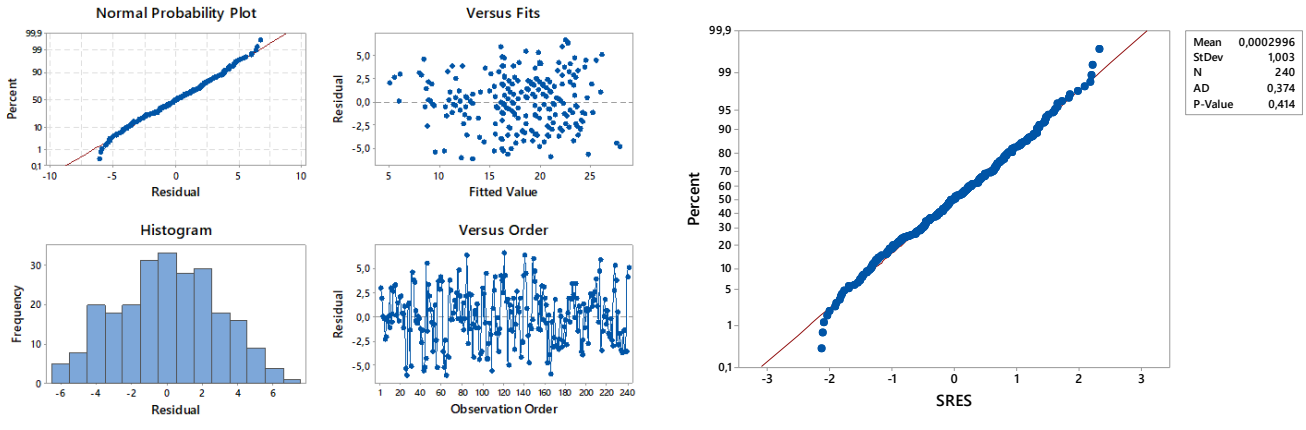
Table 3. ANOVA of experimental design.

Source	DF	Adj SS	Adj MS	F-Value	p-Value
Regression	15	5141.85	342.790	39.81	0.000
x_1	1	704.79	704.793	81.86	0.000
x_3	1	164.15	164.146	19.06	0.000
x_1^2	1	486.97	486.969	56.56	0.000
x_2^2	1	381.25	381.254	44.28	0.000
x_3^2	1	118.54	118.544	13.77	0.000
x_1x_3	1	57.56	57.558	6.68	0.010
x_1^3	1	323.47	323.468	37.57	0.000
x_3^3	1	61.73	61.733	7.17	0.008
x_4^3	1	66.55	66.555	7.73	0.006
$x_1^2x_2$	1	36.69	36.695	4.26	0.040
$x_1x_2x_3$	1	62.23	62.229	7.23	0.008
$x_2^2x_4$	1	92.79	92.787	10.78	0.001
$x_2x_3^2$	1	33.63	33.633	3.91	0.049
$x_2x_4^2$	1	84.31	84.310	9.79	0.002
$x_3^2x_4$	1	65.12	65.118	7.56	0.006
Error	224	1928.65	8.610		
Total	239	7070.50			

Table 4. Model summary adjusted in Equation (8).

R^2	R^2 (Adjust.)	R^2 (Predict.)
72.72%	70.90%	68.51%

The analysis of the standardized residuals derived from the model specified in Equation (8) indicates that they conform to a normal distribution, as illustrated in Figure 5. This conclusion is supported by the p-value obtained from the hypothesis test, which is 0.414. Since this p-value is more significant than the significance level, it confirms the normality of the residuals ($\alpha = 0.05$).



(**a**) (**b**)

Figure 5. Standardized residuals plot (**a**) and normality test (**b**) of the fitted model in Equation (8).

The surface plot modeling the response suggests that sulfation exhibits an increase at low to intermediate levels of the sampled parameters. The analysis indicates that maximum sulfation is attained at approximately 60 h across all time combinations (refer to Figure 6a–c).

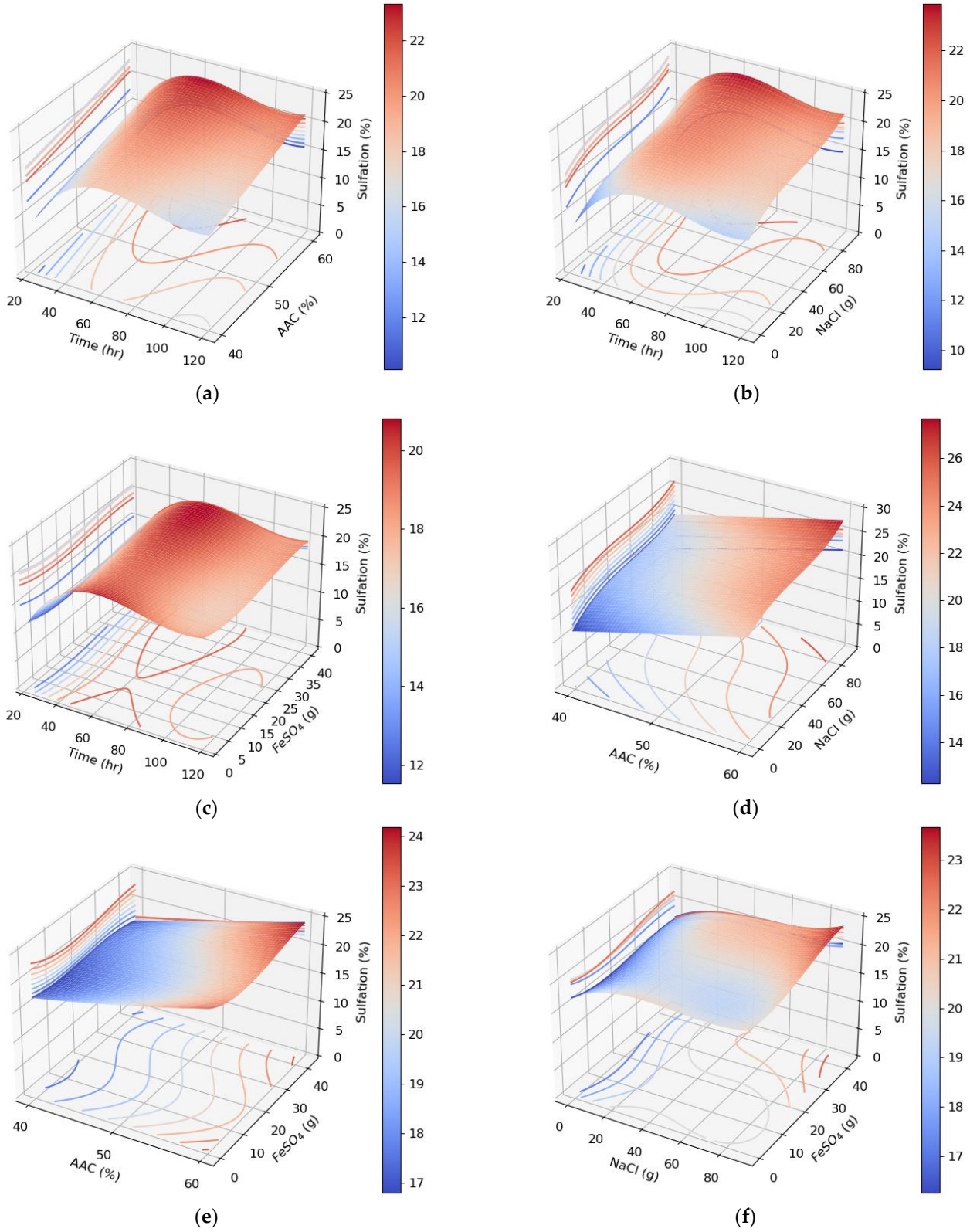


Figure 6. Response surface plot for sulfation versus: time and ACC (**a**); time and NaCl (**b**); time and $FeSO_4$ (**c**); AAC and NaCl (**d**); AAC and $FeSO_4$ (**e**); and NaCl and $FeSO_4$ (**f**).

In contrast, the response plots illustrated in Figure 6d–f demonstrate a corresponding increase in sulfation when the other independent variables examined occur in elevated levels. A directly proportional relationship is observed between the percentage of sulfation and the variables ACC, NaCl, and $FeSO_4$.

3.4. Response Optimization

By optimizing the response for the analytical model (see Equation (8)) that demonstrates sulfation using the L-BFGS-B method, the optimal response for the regression model is approximately 27.95%. Table 5 presents the factors at the optimum level.

Table 5. Values of the independent variables at the optimal level.

Variable	Optimal Value
x_1	60.14
x_2	60
x_3	90
x_4	42

Note that the time at the optimal level is not given by the highest level of the variable (eq), which is approximately 60.14 h. The highest level of sulfation is reached when the analytical consumption of acid, NaCl, and $FeSO_4$ are at their maximum.

4. Conclusions

The present investigation focused on the dynamics of a black copper reductive leaching process, examining how time, AAC, NaCl, and $FeSO_4$ influence sulfation. The key findings can be summarized as follows:

- The study successfully modeled complex sulfation dynamics associated with the pretreatment of copper ores with black oxides, utilizing multivariate nonlinear regression models;
- The experimental design and response surface methodology proved valuable tools for analyzing sulfation behavior in regards to variations in independent variables;
- An exploratory analysis, validated by main effects analysis, revealed that the relationships between the independent variables—analytical acid consumption (AAC), NaCl, and $FeSO_4$—are directly proportional to sulfation across the entire sampled domain;
- Time was found to have a statistically significant effect only within the 24–48 h variation, with no significance observed in other comparisons;
- Analytical acid consumption exhibited a consistent positive gradient for sulfation throughout the domain, maintaining statistical significance at all levels sampled;
- While the presence of NaCl was statistically significant, the substantial effect was noticed when comparing the tests without chloride and with the maximum addition of NaCl;
- No statistically significant differences were detected among the levels of $FeSO_4$ sampled;
- The regression model developed to represent sulfation demonstrated a beneficial statistical fit, with a marginal difference between the fitted and predicted coefficients of determination, indicating its reliability as a predictive tool;
- The model optimization identified optimum sulfation values around 60 h, with an analytical acid consumption of 60%, 90 g of NaCl, and 42 g of $FeSO_4$.

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