

## Article

# Extraction of Phosphorus from Sewage Sludge Ash—Influence of Process Variables on the Electrodialytic Process

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**Abstract:** Phosphorus is a critical, irreplaceable raw material, and developing methods to recover P from secondary sources such as sewage sludge ash (SSA) is crucial. Two-compartment electrodialytic extraction (2C-ED) is one method where an electric DC field is applied to extract P and separate heavy metals simultaneously. Several process parameters influence 2C-ED, and they influence each other mutually. This paper explores chemometrics modeling to give insight into the 2C-ED process and, specifically, optimization of the experimental parameters towards 80% P extraction. A projections-to-latent-structures model was constructed based on new 2C-ED experiments conducted with one SSA type. The model was stable (high correlation factor and predictive power). Variable importance in the projection (VIP) plots showed that the influence of the variables was in the order: current > duration > L:S ratio > stirring velocity > dispersion solution (weak acid or distilled water). Contour plots were used for exploring different P extraction strategies. For example, more P mass per unit current was extracted at an L:S ratio of 7 compared to L:S 14. This shows that treating a thicker SSA suspension is preferable to optimize the current efficiency. The chemometric model proved valuable for optimizing the 2C-ED process and future scale-up.

**Keywords:** phosphorus; heavy metals; electrodialysis; projections to latent structures; extraction



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## 1. Introduction

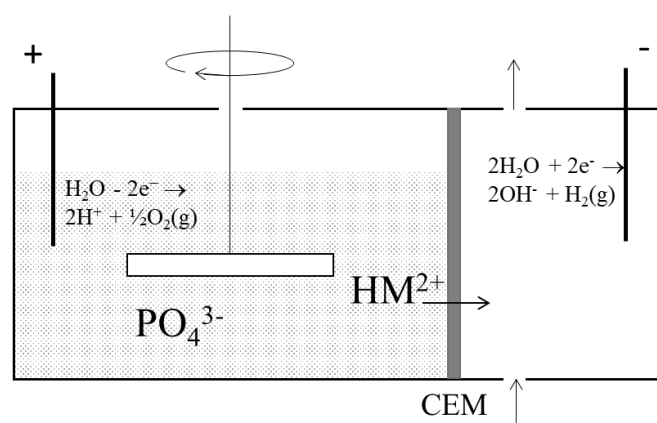
Phosphorus (P) is on the EU list of critical raw materials [1]. With an expanding global population relying on decreasing and deteriorating P resources, the development of technologies for improved P recovery is becoming an increasingly urgent environmental, economic, and societal issue [2].

Sewage sludge incineration is practiced widely in some European countries [3], where legislative developments prohibit the direct spreading of sewage sludge on agricultural land and require mandatory P recovery from the SSA. Wet extraction of P in acid has been extensively studied [4], and high P extraction percentages can be obtained (80–100%) [5,6]. The acid demand for extraction of P from SSA is high. The SSAs generally have a high pH (about 10 [7]) and the pH in the leachate needs to be below about 2 [5] in some ashes and even about 1 in others [7]. An example of the acid demand is given in [6], where an optimized process showed that for 80–100% P extraction from 1 tonne of SSA, the acid used was 368 kg of 98% H<sub>2</sub>SO<sub>4</sub>. Handling and transporting such high amounts of acid is not straightforward in all urban settings. In addition, the simultaneous extraction of heavy metals and P [6,7] necessitates a second step for the separation to support the European Green Deal, which promotes the recycling of finite resources but simultaneously emphasizes a zero-pollution ambition. Thus, there are challenges related to the acid extraction of P from SSA, which support the development of alternative technologies.

One such alternative under development is electrodialytic extraction in a two-compartment cell (2C-ED) [8], which is a one-step process for simultaneous P extraction and heavy metal

separation. The process is driven by an applied electric DC field. During 2C-ED extraction, the hydrogen ions causing the acidification are produced by electrolysis at an anode, which is placed directly in the SSA suspension. Advances in Power-to-X (PtX) processes are progressing quickly, using concepts based on utilizing renewable electricity to produce hydrogen gas through water electrolysis [9]. Harvesting the DC current for the electrolysis in 2C-ED extraction directly from photovoltaics or wind may be an option. If, in addition, the hydrogen gas produced during the 2C-ED is collected and utilized as suggested in [10], the overall environmental footprints for the process can be minimized.

In Denmark, the government's resource strategy has since 2013 targeted a minimum of 80% P recovery from sewage sludge [11], which sets the optimization criteria for P extraction in this and previous work on 2C-ED. A proof of concept for the 2C-ED (Figure 1) was given in [8]. The method has been tested for the extraction of P from batches of SSA originating from three different fluidized bed mono-incineration plants (see Supplementary Materials Section S1). Regardless of variations between the SSA characteristics, the 2C-ED extraction and separation proceeded successfully.



**Figure 1.** Principle of the two-compartment electrochemical cell (2C-ED). (HM = heavy metals; CEM = cation exchange membrane). P remains in the dispersion solution of the SSA suspension.

Following proof of concept is process optimization. Previous work on 2C-ED for P recovery and heavy metal separation has been published in six papers (listed in Supplementary Materials Section S1). In these papers, the influences on the process from five different important process variables were investigated separately. However, as the variables must be expected to influence each other, it is necessary to optimize them mutually, which is the focus of the present work.

### 1.1. Principle of 2C-ED Extraction

The principle of 2C-ED extraction in a two-compartment cell for the simultaneous extraction of P and separation of heavy metals is illustrated in Figure 1.

The anode is placed in the SSA suspension and the acidification of the suspension from the electrolysis at the anode ( $\text{H}_2\text{O} \rightarrow 2\text{H}^+ + \frac{1}{2}\text{O}_2(\text{g}) + 2\text{e}^-$ ) causes extraction of heavy metals and P. A cation exchange membrane (CEM) separates the SSA suspension and the catholyte. The CEM is a semipermeable membrane and it is a selective barrier permeable to cations. The applied electric field is carried by electromigrating ions in the dispersion solution and catholyte, and, with the CEM between the two compartments, the electric current is mainly carried by cations from the dispersion solution into the catholyte. That is, the positively charged heavy metal ions electromigrate into the cathode compartment, whereas P remains dissolved in the dispersion solution as neutral or negatively charged compounds ( $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ , or  $\text{PO}_4^{3-}$ ) dependent on the prevailing pH. Hereby, simultaneous P extraction and heavy metal separation are obtained. The heavy metal content relative to P in the dispersion solution has been shown to meet the limiting values for the use of industrial wastes as fertilizers; thus, the filtrate is ready for processing into P fertilizer [12].

Such processing could involve precipitation by neutralization, such as the process described in [4]; however, the optimal method remains to be identified.

The extraction of the target elements from the acidification by electrolysis does not selectively target P and heavy metals, which means that other chemical elements are also extracted. Dissolution of the P-containing particles also results in the release of the other elements in these particles, e.g., Ca from calcium phosphates, which was seen to dissolve during 2C-ED in [13]. The extracted Ca will electromigrate as cations into the catholyte. From the acid extractions in [7], it is known that Al (another major element in SSA) also dissolves from the SSA by acidification. Al is interesting to explore further in the 2C-ED process because it can precipitate or form charged compounds with the extracted P. Even though such precipitation does not hamper the 2C-ED extraction and separation process, it might have an influence, which should be taken into account.

It is advantageous to consider the added value from the potential utilization of the residual SSA after P extraction [14]. A strength of 2C-ED is that the SSA is suspended in water, i.e., no new ions or chemicals are introduced, which supports further utilization. Based on test productions, it was seen that the treated SSA can potentially be used as a partial replacement for cement in concrete [15] or a partial clay replacement in fired clay bricks [13]. To be successful, the produced construction materials should have equivalent properties to the references without treated SSA, and they should not pose any risk for leaching of heavy metals. Test castings of mortar specimens with 20% cement replaced with 2C-ED-treated SSA [15] showed a loss of 9% in compressive strength, but as the workability of the mortar was decreased as well (and not adjusted for), this result might be improved. Small brick test discs were fired with 10–50% clay replacement with 2C-ED-treated SSA [13] and the results showed that, when fired at 1000 °C, all brick discs had apparent densities and open porosities within the accepted range of bricks used in the building industry. Thus, the first results were encouraging, but more tests are needed both on the material properties and leaching. Thus, 2C-ED separates the SSA into a P resource with low heavy metal content and a particulate material, which has the potential to be utilized in construction materials.

### *1.2. Chemometric Modeling of ED*

The present work uses chemometric modeling, both descriptive (to evaluate the influence of variables) and predictive (to optimize different experimental variables) in relation to 2C-ED. PLS (projections to latent structures) models investigate possible links between two data matrices; X (the experimental variables in the experiments) and Y (the responses, i.e., the extraction and separation results). Chemometrics has been shown to be a valuable tool concerning the optimization of process variables for ED remediation of e.g., [16].

### *1.3. Aim of Work*

This work applies chemometrics to provide insight into the 2C-ED process and to optimize the experimental variables in the 2C-ED method for simultaneous P extraction and heavy metal separation from SSA. The 2C-ED process is driven by the applied current, and optimization of the process involves efficient use of the applied current.

The aim of this work is to assess the influence of the experimental variables, identify possible correlations between the variables and extraction/separation results, and enable mutual optimization of the experimental variables. The ultimate goal is to provide inputs to scale up the ED separation process.

## **2. Materials and Methods**

### *2.1. Experimental Procedures*

#### *2.1.1. Investigated SSA*

The investigated SSA was from the mono-incineration plant of Avedøre Wastewater Service, Denmark (a fluidized bed combustor, 850 °C). The incinerator has an average daily production of 7–8 tonnes of SSA. The wastewater treatment plant uses Kemira PIX-118

with iron chloride sulfate to precipitate phosphates into the sludge, and, accordingly, the Fe content in the SSA is high. The SSA used was the fly ash collected at electrostatic filters. It was not mixed with flue gas purification products from the bag filters.

### 2.1.2. SSA Characterization

Concentrations of Al, Ca, Cu, P, and Zn were measured after digestion of the SSA according to the US EPA 3015A method [17] with a Varian 720-ES ICP-OES (inductively coupled plasma-optical emission spectrometer). Initial concentrations were measured for nine replicates, sampled from different positions in the 10 kg sample. The pH of the SSA was measured in a suspension of 10.0 g SSA in 25 mL distilled water with a Radiometer pH electrode after 1 h of agitation and a few minutes of settling (five replicates). Solubility in water was evaluated (in duplicate) after the process described in [7].

### 2.1.3. ED Laboratory Experiments

A cylindrical 2C-ED laboratory cell was used. The dimensions were the same as in previous works, e.g., [12]. The internal diameter was 8 cm. The length of the compartment with the SSA suspension was 10 cm. The cathode compartment was 5 cm long. A cation exchange membrane from IONICS (3009753) separated the two compartments. The electrodes were platinum-coated titanium wires (diameter 3 mm) from Permascand®, and they protruded 5 cm horizontally into the cell compartments. A Hewlett Packard E3612A power supply supplied a constant current. The catholyte (500 mL 0.01 M NaNO<sub>3</sub> adjusted to pH 2 with HNO<sub>3</sub>) was continuously circulated between the cell compartment and a flask. Once each day, the pH in the catholyte was manually adjusted to between 1 and 2 with 1:1 HNO<sub>3</sub> (the pH was checked by measurement 30 min after the adjustment). The SSA was suspended in either distilled water or HNO<sub>3</sub> (Table 1). In every experiment, the SSA was suspended in 350 mL liquid, and the L:S ratios (7, 10, or 14) were adjusted by varying the mass of SSA (50 g, 35 g, or 25 g dry SSA, respectively). The SSA was kept suspended by an overhead stirrer (InVitro in the experiments with 100 and 250 rpm or VWR VOS 14 for 500 rpm).

**Table 1.** The experimental 2C-ED design. Experiments 1–10 were screening experiments, and experiments 11–18 were additional experiments used in the improved model. Experiments 19 and 20 were used for model verification.

	Exp.	Current (mA)	Duration (Hours)	Stirring (rpm)	L/S	Distilled H <sub>2</sub> O (D) or M HNO <sub>3</sub> (S)
Screening experiments	1	0	48	500	14	D
	2	60	48	100	14	S-0.005
	3	0	168	100	14	D
	4	60	168	500	14	S-0.005
	5	0	48	500	7	S-0.005
	6	60	48	100	7	D
	7	0	168	100	7	S-0.005
	8	60	168	500	7	D
	9	30	120	250	10	D
	10	30	120	250	10	S-0.005
Additional experiments for the extended model	11	60	48	500	14	S-0.01
	12	60	48	100	14	S-0.01
	13	60	168	500	14	S-0.01
	14	60	240	100	14	D
	15	100	72	100	7	D
	16	100	168	250	7	D
	17	50	168	500	7	D
	18	75	168	500	7	D
Experiments for model verification	19	60	168	250	14	D
	20	100	120	500	7	D

At the end of the ED experiments, the suspension was filtered. The contents of Al, Ca, Cu, P, and Zn were measured in the SSA, solutions, cation exchange membrane, and on the cathode. The removed part of the elements into the cathode was the sum of what was found in the catholyte and CEM and precipitated on the cathode. Before the measurement of concentrations using a Varian 720-ES ICP-OES, the selected elements were extracted from the SSA by the US EPA 3015A method [17]. The contents in the cation exchange membrane were measured after extraction in 1.0 M HNO<sub>3</sub> for 24 h. Rinsing of the cathode before the measurement was carried out in 5.0 M HNO<sub>3</sub> for 24 h. The acid concentrations for extracting the elements from the ion exchange membrane and rinsing of the cathode were chosen from experience that showed that these acids will release close to all of the elements to the solution for the measurements. In Section 3, the mass percentages in the dispersion solution are marked (+), the mass percentages in the cathode compartment (sum of mass in cation exchange membrane, catholyte, and electro-precipitated on the cathode) are marked (-), and the mass percentages remaining in the SSA are marked (SSA).

## 2.2. Multivariate Analysis—PLS Modeling

The present work is inspired by the three-step methodology of PLS (projections onto latent structures) modeling for electrodialytic remediation of harbor sediment [16]. A PLS model (named the extended model in this paper) was built through an iterative process. Literature data were collected; however, the data were too limited to produce a chemometric model (see discussion in Supplementary materials Section S1), and the experimental variables for a screening model were selected on the basis of experiments reported in the literature. From the screening model, additional experiments were designed to produce the extended model, which formed the basis for the descriptive and predictive findings.

### 2.2.1. PLS Model Based on Literature Data

A screening of the literature for ED extraction of SSA was undertaken. The PLS model developed from the literature data was based on only 2C-ED experiments because [18] showed that 2C and 3C ED set-ups should be considered as different systems when applying chemometric modeling to the treatment of other polluted materials. SSA characteristics vary depending on the wastewater treatment plant and the incineration regimes [19]. Since the model based on the literature study indicated that variations in the SSA characteristics were at a level that influenced the 2C-ED separation result, it was decided to design the experimental series with SSA from the same plant and batch.

### 2.2.2. Choice of Experimental Variables and Responses for Screening Model

The choice of experimental variables for the screening experiments was based on findings from the literature. Current and duration had the strongest influence on the ED of harbor sediments [16] and were selected as experimental variables in the current work. Continuous stirring vs. non-stirring has previously been shown to influence the P extraction as 90% and 20% P were extracted from SSA in two otherwise similar 2C-ED experiments [20]. Stirring velocity was selected as a variable in the current work. Suspending the SSA in H<sub>2</sub>SO<sub>4</sub> increased the rate of P extraction [21]; however, to avoid adverse impacts on the residual ash related to utilization in construction materials, HNO<sub>3</sub> might be a better option. Further, 2C-ED has the environmental advantage of utilizing electrolysis rather than chemicals, and, accordingly, a dispersion solution of distilled water or acid (compared to [21]) was selected.

The selected values for the experimental variables were: current (0, 30, or 60 mA), duration (38, 120, or 168 h), stirring velocity (100, 250, or 500 rpm), L:S ratio (7, 10, 14 mL/g), and distilled water or 0.005 M HNO<sub>3</sub> (discrete variable, i.e., one or the other).

The chosen responses were the mass loss of SSA (g), the final pH of SSA, and the percentage of Al, Ca, Cu, P, and Zn in (i) the SSA, (ii) the dispersion solution, and (iii) the cathode compartment. Al and Ca were included because of their expected importance for the process. The importance of Al in acid extraction processes was e.g., reported in [22]



where they identified  $\text{AlPO}_4$  in the SSA, which was partly dissolved in HCl and then precipitated again on the surface of the solid phase. Ca has been shown to represent a significant mass percentage in the SSA, and calcium phosphates have been identified in SSAs (also in SSAs from the same incineration plant [15]).

#### 2.2.3. Fractional Factorial Design for the Screening Model

A factorial design can help determine the influence of the experimental variables and the possible interaction effects between them in 2C-ED processes [16]. Undertaking a complete two-level factorial design would entail conducting  $2^5$  (32) experiments. Assuming that the interaction effects between three, four, five, or six factors are negligible, the number of experiments can be reduced to a complete  $2^{5-2}$ , (i.e., 8 experiments) [23]; here, experiments 1–8 in Table 1. The two experiments 9 and 10, with variables close to the center of the fractional design, were added to the screening model to stabilize and verify it. The screening model had five variables and 17 responses.

#### 2.2.4. Experimental Variables in the Extended Model

Eight 2C-ED experiments additional to the screening experiments were performed to form the extended model. The reasoning for choosing the experimental design for the extended model is presented in Section 3.5.

#### 2.2.5. Overview of Conducted 2C-ED Experiments

Table 1 shows 20 2C-ED experiments. Experiments 1–10 were used to screen for variable importance in the developed PLS screening model. Experiments 11–18 expanded the original factorial design in the extended PLS model for analyzing the optimization of 2C-ED. Experiments 19 and 20 were used to verify the extended model.

#### 2.2.6. Software

The Simca 16 software was used for the PLS modeling. The models were evaluated from the correlation factor  $R^2Y$  and the predictive power  $Q^2$ .  $R^2Y$  is the cumulative fraction of the variation of the Y variable explained by the model after the last component, i.e., how well the model fits the data.  $Q^2$  is the variation in the Y variable predicted by the model, after the last component according to cross-validation, and  $Q^2$  is a measure of how well the model predicts new data. Weights plots were produced to determine the mutual relations between the variables and the responses. Variable importance in the projection (VIP) plots were used to assess the variable importance for the computed models. Contour plots were used to explore different strategies for the variables to reach 80% P extraction.

### 3. Results and Discussion

#### 3.1. Characteristics of Investigated SSA

The investigated SSA had a pH of 11.6 and a solubility in water of 3.4%. The average concentrations of the selected chemical elements were (the minimum and maximum concentrations measured are shown in brackets): Al 21.9 g/kg (21.2–22.8 g/kg), Ca 111 g/kg (96–123 g/kg), P 82.8 g/kg (78.4–86.0 g/kg), Cu 536 mg/kg (504–565 mg/kg), and Zn 2020 mg/kg (1880–2160 mg/kg). In the literature, 2C-ED experiments have been reported on SSAs from three incineration plants (two Danish and a German) (see Supplementary Material Section S1). The SSA investigated in the present work had similar characteristics (see Supplementary Materials Section S1).

#### 3.2. Overall Results from ED Experiments

The mass balance for each chemical element in a 2C-ED experiment is the total mass in the different parts of the cell at the end of the experiment (cathode, catholyte, cation exchange membrane, dispersion solution, and SSA) relative to the initial amount (based on the mass of SSA and the initial concentration). Considering variations in SSA batch concentrations, mass balances at 80–120% are considered acceptable. The difference between

the highest and lowest concentrations measured was between 7 and 24% from the average, and variation in this size will influence the mass balances. All mass balances were in this range. The percentwise distribution of a chemical element at the end of a 2C-ED experiment was calculated for the SSA, the dispersion solution, and the cathode compartment (the latter is the sum of the element in the catholyte, in the cation exchange membrane, and on the cathode). The percentage was calculated based on the total mass in the 2C-ED cell at the end of the experiment. The multivariate analysis performed used the percentwise distribution since the target was to extract 80% P into the dispersion solution.

The experimental results are shown in the Supplementary Materials (Section S2) as the final pH of the SSA (which ranged from 2.5 to 5.3), the dissolved mass of SSA (7–51%), and the percentwise distribution of the five investigated chemical elements (Al, Ca, P, Cu, and Zn). The percentwise distributions in the 20 2C-ED experiments are shown in Figure 2.

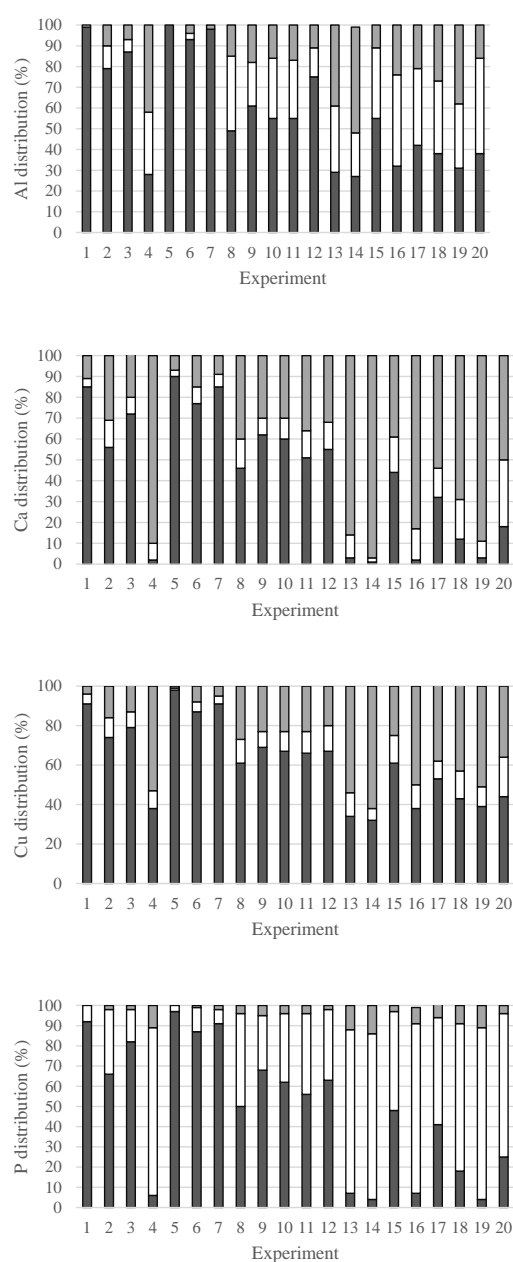
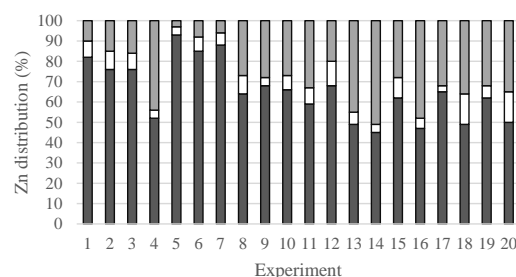


Figure 2. Cont.



**Figure 2.** Distribution of Al, Ca, Cu, P, and Zn in the 2C-ED cell at the end of the experiment. (SSA ■, dispersion solution (+) □, cathode compartment (−) ▒).

The majority of the extracted Ca, Cu, and Zn was in the cathode compartment, and the majority of P was in the dispersion solution. Thus, P and the heavy metals were separated as intended. The Al was distributed in both the dispersion solution and the cathode compartment with no clear separation.

Less than 10% P remained in the SSA after five of the 2C-ED experiments (exp. 4, 13, 14, 16, and 19). In these experiments, about 28–32% Al, 1–3% Ca, 32–60% Cu, and 45–62% Zn remained in the SSA, which shows that the P and Ca were the most readily dissolved from the SSA during the 2C-ED experiments. The five experiments with the highest extraction of Ca and P had final pH below 3.7 (see Supplementary Materials Section S2). Whitlockite ( $\text{Ca}_9(\text{PO}_4)_6\text{PO}_3\text{OH}$ ) is a common P-bearing mineral in SSA, and it is soluble in acid [6]. Dissolution of whitlockite constitutes a part of the Ca and P extraction. The highest mass loss of the SSA (51%) was found for exp. 14, which was also the experiment with the highest extracted percentage of the investigated elements (Figure 2), i.e., 72% Al, 99% Ca, and 96% P. These percentages with the initial concentrations in the SSA (Section 3.1) accounted for about 21% of the mass loss, i.e., many other chemical elements were released from the SSA during the extraction. Since the 2C-ED method does not selectively extract the target elements, it is important to stop the process at the time when the demanded P extraction is reached since a loss of the efficient use of the applied current will follow. The particles that are not dissolved during 2C-ED are quartz, hematite, and feldspars [13]. Some Cu and Zn-containing particles were not soluble in the 2C-ED experiments since at least 32% Cu and 62% Zn remained in the SSA after the treatment.

### 3.3. PLS Model Based on Literature Data

The 2C-ED experiments reported in the literature were conducted with SSAs from three different plants. There was too little data to develop a PLS model for the three SSAs. Accordingly, SSA characteristics were included to account for any variability between the SSAs. The model had the correlation factor  $R^2Y = 0.512$  and the predictive power  $Q^2 = 0.475$ . The model indicated that variations in the SSA characteristics influenced the 2C-ED result, and it was decided to design the experimental series in the current work with the same SSA to focus on the influence of the experimental variables on the P extraction and heavy metal separation.

### 3.4. PLS Screening Model

Experiments 1–10 (Table 1) were the basis for the PLS screening model. The screening model had one component,  $R^2Y = 0.745$ , and  $Q^2 = 0.373$ . Thus, the model summary was much better than the model based on the literature data. The chosen experimental variables in the screening experiments did not sufficiently cover the relevant experimental domain concerning the responses. Only experiment 4 fulfilled the target of 80% P in the dispersion solution after ED (Figure 2).



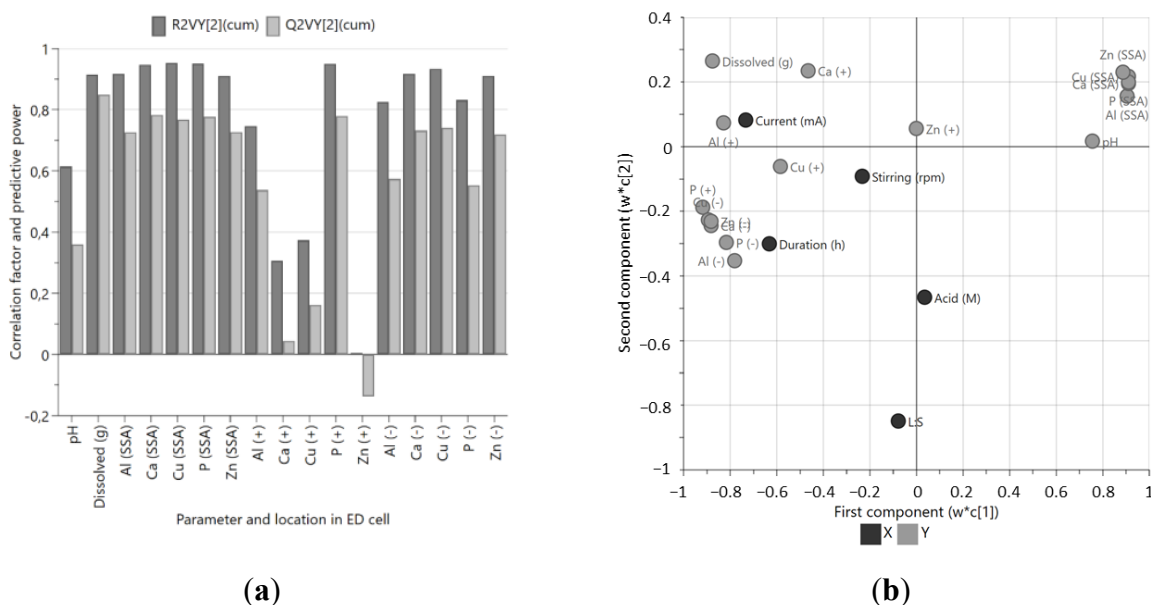
### 3.5. Extended PLS Model

The experimental variables for the eight additional experiments were chosen based on the results from the screening experiments to extend the model and make it applicable for the optimization of the 2C-ED process:

- Experiments 11–13: Suspending the SSA in acid had a minor influence in the screening model (Supplementary Materials Section S3). Suspending the SSA in 0.01 M HNO<sub>3</sub> (twice as strong) was included to see if this (still weak) acid enhanced the process. Experiment 14: this had a longer duration than the screening experiments to have more experiments in the model, fulfilling the response criteria of 80% P extraction.
- Experiments 15–16: these had a higher current (100 mA) than the screening experiments ( $\leq 60$  mA) to extend the covered area for current as a variable.
- Experiments 17 and 18: additional experiments focusing on different currents within the experimental domain.

The other experimental variables to those specifically selected and listed above were chosen from the values that were also used in the screening experiments.

The extended PLS model had  $R^2Y = 0.765$  and  $Q^2 = 0.510$ , i.e., a slightly higher  $R^2Y$  and significantly higher  $Q^2$  than the screening model, meaning it was more stable and that, accordingly, it can be used with higher certainty. It had two components. The PLS model summary for the extended model (Figure 3a) covered all the responses well, except for Ca, Cu, and Zn in the dispersion solution (which was consistent with the PLS model summary for the screening experiments (Supplementary Materials Section S3)). The percentages of these three elements in the dispersion solution at the end of the experiments were Ca (2–19%), Cu (1–14%), and Zn (4–15%). For comparison, the percentage of P in the catholyte was 0–14%. Since P(-) is covered well by the model, it indicates that the range of the responses is not problematic. It is, rather, that the selected experimental variables do not correlate with these three elements in the dispersion solution or that these responses cannot be modeled in the chosen domain of the variables.



**Figure 3.** (a) PLS model summary plot for the extended model (correlation factor  $R^2Y$  and predictive power  $Q^2$ ), and (b) weighted plot for the improved model.

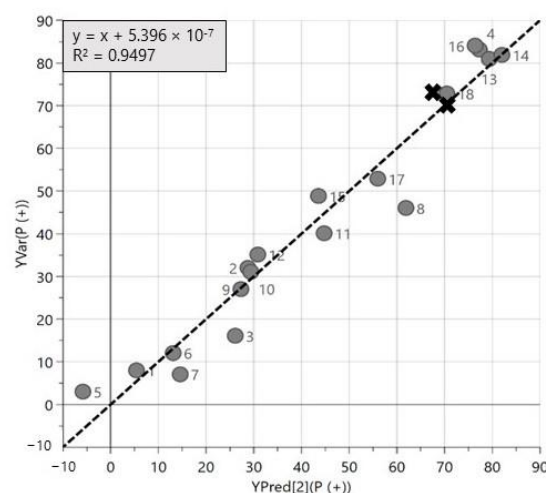
The weighted plot (Figure 3b) relates the experimental variables and the responses. The pH and the percentages in the SSA were placed closely together, showing that the lower the pH, the lower the quantity of the measured elements were left in the SSA. As expected, the percentages of all the elements in the catholyte and P in the dispersion solution were placed directly opposite the elements remaining in the SSA.

The final pH of the SSA had almost no influence on the second component ( $w^*c[2]$ ). At the same time, the L:S and acid concentration of the initial dispersion suspension only influenced the second component (very close to the  $w^*c[1]$ -axis). Thus, these two variables did not influence the pH of the SSA. This, combined with the percentage of the investigated elements left in the SSA being influenced by both the first and second components, showed that the extraction of these elements was not solely linked to the final pH of the SSA. This is in line with a finding in [24] concerning the ED of soil. The authors of this study found that ED obtained higher extraction than acid-leaching, even when the pH during the acid-leaching was lower than the final pH in the dispersion solution. Thus, the ED extraction depends on more than the pH in the suspension, which underlines that it is a complex method, and that mutual optimization of experimental variables is advisable.

VIP plots (Supplementary Materials Section S4) reflect the importance of the variables in the extended PLS model. The order observed was: current (1.59) > duration 1.36) > L:S (0.54)  $\geq$  stirring (0.51) > acid concentration (0.30). The applied current and the duration had a major influence on the responses (which is in accordance with [16] for the electrodialytic remediation of harbor sediments). The acidification of the SSA suspension depends on these two factors. The charge transfer through the cell (current times duration) determines the number of protons produced by electrolysis at the anode. The current determines at which rate the protons are formed. That the current was more important than the duration indicates that the rate with which the protons are formed is slightly more important than the total amount of protons formed in the investigated experimental domain.

### 3.6. Predicting P Extraction

As the primary aim of 2C-ED of SSA is to extract P into the dispersion solution, it is interesting to consider the ability of the extended model to predict this response. The PLS model summary (Figure 4) showed that, when focusing on P(+), the extended model had  $R^2Y = 0.949$  and  $Q^2 = 0.779$ , i.e., a good model with high predictive power. Figure 4 shows the predicted (YPred) vs. the measured (YVar) percentage of P in the dispersion solution. The two additional experiments 19 and 20 (Table 1), undertaken to verify how well the extended model predicted the response of the new experiments, are marked with crosses. The model predicts the P extraction in these two experiments well.



**Figure 4.** Observed (YVar) vs. predicted (YPred) values for the percentage of P in the dispersion solution (the 1:1 line is marked as a dotted line). The numbers refer to experiments. The two black crosses show the results of the verification experiments.

An important use of the model is to choose variables resulting in a +80% P extraction into the dispersion solution. Such high P extraction was obtained in experiments 4, 13, 14, and 16, and the model predicted the experimental values at this level relatively well (Figure 4). The P extraction results for exp. 13 and 14 were on the 1:1 line between the

predicted and measured percentages. However, for experiments 4 and 16, the model slightly underestimated the extraction (measured recoveries 83 and 84% vs. estimated recoveries 77 and 76%). If a better prediction is desired around the 80% extraction, it may be necessary to produce a PLS model that focuses on the space for the responses at, for example, more than 70% extraction. Previous work [12] with 2C-ED showed that the extraction rate for P decreases when approaching a full extraction. The 2C-ED process for P extraction generally follows the phases described in [12]. There is a lag phase where the buffering capacity of the SSA hinders the acidification of the suspension. The second phase starts when the buffering capacity is eliminated, and the extraction rate is subsequently high. In the third phase, the extraction rate decreases as the P concentration in the SSA decreases, and the fraction hardest to extract is the one left. Narrowing the domain for responses to the third phase would probably enable a more precise P extraction prediction. In addition, the predicted percentages of Ca, Cu, and Zn in the dispersion solution (which are not covered by the current model, Section 3.5) might also be covered by the model if the domain was narrowed for the same reasons.

### 3.7. P Extraction Strategy

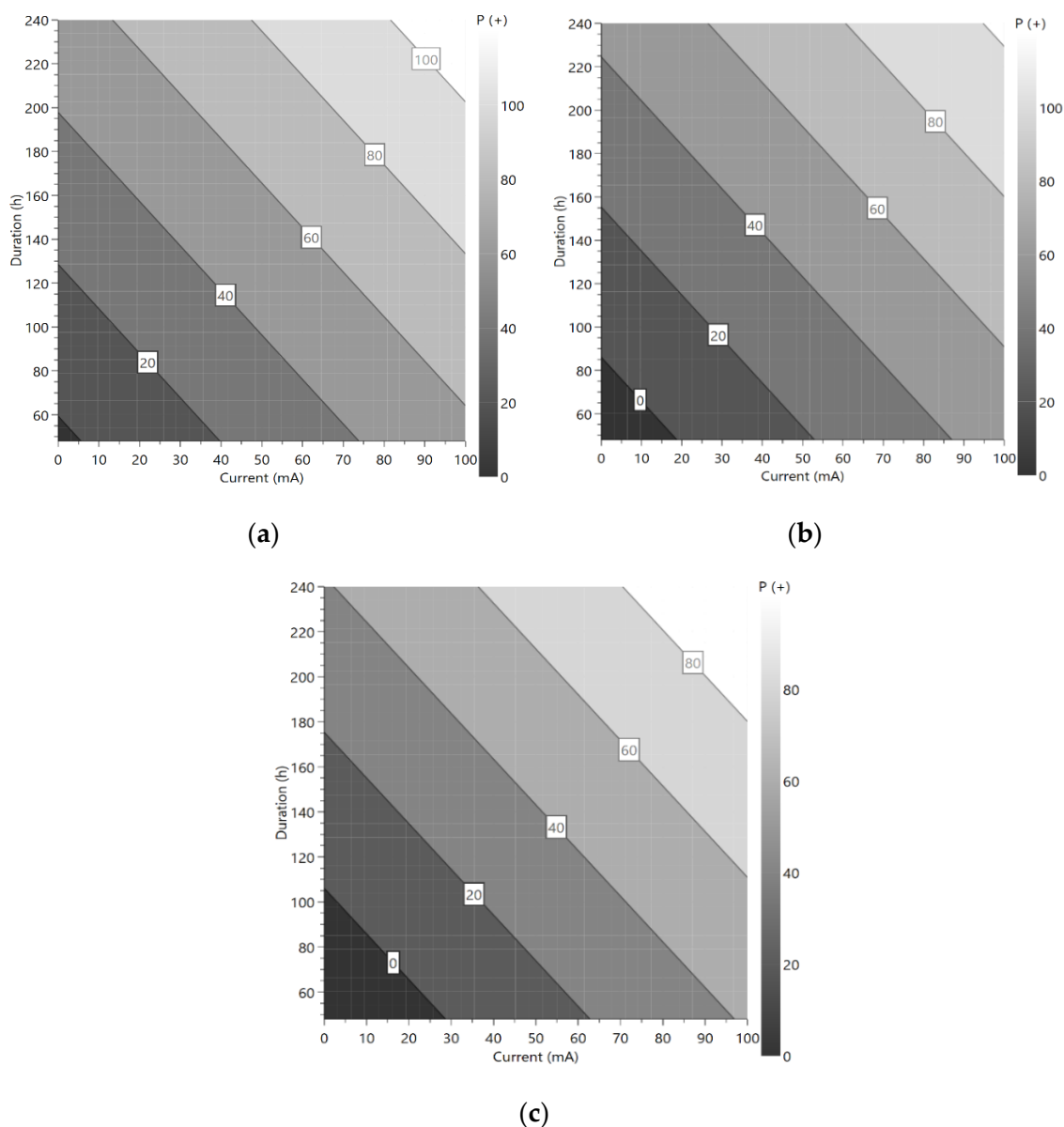
It is interesting when considering the most efficient use of the applied current and future plant design to explore further the differences in treating the SSA at a high or low L:S. For this purpose, three contour plots were constructed with different L:S (7, 10, and 14) showing the extracted percentages in the duration–current space with the same stirring rate (250 rpm) (Figure 5a–c).

From these contour plots, it was possible to compare the influence of the L:S ratio (hereby, the mass SSA treated as differences in the LS: ratio was achieved by adjusting the mass of SSA in the cell) on the duration to +80% recovered P. For example, with an applied current of 75 mA, the duration for recovering 80% P was found to be 185 h at L:S 14 (25 g SSA), 215 h at L:S 10 (35 g SSA), and 230 h at L/S 7 (50 g SSA). Thus, there was no linear relation under these chosen settings. At 250 rpm and 75 mA, it will take 185 h to recover 80% P from 25 g SSA (L:S 14), but only 45 h more to recover the same percentage from 50 g SSA (L:S 7). The finding that the 2C-ED extraction process was most efficient at a high L:S ratio is contrary to findings for batch acid extractions. Here, the leaching of P increases with the L/S ratio [22]. A low L:S ratio during 2C-ED is desirable since the two factors, L:S and duration, determine a treatment plant's size. Understanding of the preferable treatment of a low L:S ratio solution requires reflection concerning upscaling 2C-ED extraction, e.g., whether an overhead stirrer is the best option for keeping the ash in suspension.

The concentration of P in the dispersion solution will be higher the lower the L:S ratio (at the same extraction percentage), which means a smaller volume of dispersion solution to process. At an L:S ratio of 7 and 80% extraction of the 83 g P/kg SSA, the concentration in the dispersion solution would be approximately 9 g P/l, corresponding to 2.8%  $\text{H}_3\text{PO}_4$ . From the dispersion solution, a precipitation step, possibly precipitation of calcium phosphate, is needed to produce a commercial product. The status of the protons might explain the beneficial choice of treating a low L:S suspension from the electrolysis at the anode. It is important to distinguish between the protons which are current-carrying into the catholyte and protons which react with the particulate material [25]. Protons have a higher ionic velocity than other cations. The nature of the reactive and current-carrying protons in ED can explain the influence of the L:S ratio on the extracted percentage of P. More reactive protons would be expected at a higher L:S ratio. The current-carrying protons contribute to lower resistivity but are not directly involved in the P extraction and heavy metal separation [25]. On the other hand, the reactive protons acidify the SSA, causing extraction of the P and heavy metals. Thus, in order to have the highest efficiency of the applied current, these results suggest that treating a suspension of low L:S is optimal.

The ED extraction process is more time-consuming than acid extraction, meaning that a larger plant is needed to treat the same amount of SSA (if the same L:S ratio is used). This issue must be addressed in subsequent developments. If the L:S is lowered, the plant

size needed decreases accordingly. The lowest L:S ratio tested in this work was 7, and the best results were obtained at this L:S. This is encouraging in order to operate the 2C-ED at an even lower L:S ratio; however, at a lower L:S ratio an overhead stirrer, as used in the laboratory cells to keep the SSA suspended, may not be the best option, and a new design of the 2C-ED is needed when scaling up the process. The new design should also preferably support the treatment of the SSA in a continuous process to ease the operation. In the new design the movement of the SSA involves a continuous process and keeping the SSA in suspension can be combined. Increasing the current is also an option for decreased duration of 2C-ED, which should be explored. However, 2C-ED is a process that must be expected to last a few days. At full scale, one can imagine that the 2C-ED extraction unit would be placed next to the sewage sludge incinerator to minimize the transport of the SSA. Future work should focus on mutually optimizing the L:S, current, and duration to achieve the fastest process at the highest current efficiency. The work should include lower L:S ratios and higher currents than were included in the investigated experimental domain, which seems possible from the obtained results.



**Figure 5.** Contour plot with current and duration (stirring 250 rpm). (a) L:S 14 (25 g SSA), (b) L:S 10 (35 g SSA), and (c) L:S 7 (50 g SSA).

### 3.8. Separation of Al, Ca, Cu, and Zn

The extended model can predict the separation of Cu ( $R^2Y = 0.933$ ;  $Q^2 = 0.718$ ) and Zn ( $R^2Y = 0.911$ ;  $Q^2 = 0.718$ ) into the cathode compartment. This is useful in designing strategies for handling heavy metals after the 2C-ED, e.g., further extraction or precipitation for safe disposal. The PLS model also predicted the extraction and the separation of Ca into the cathode compartment well ( $R^2Y = 0.918$ ;  $Q^2 = 0.732$ ).

The extracted Al was more equally distributed in the cathode compartment and dispersion solution than the other investigated elements (Figure 2). The percentage of Al extracted was modeled relatively well: in the dispersion solution ( $R^2Y = 0.746$ ;  $Q^2 = 0.537$ ) and in the cathode compartment ( $R^2Y = 0.825$ ;  $Q^2 = 0.574$ ) (Figure 3a). The weighted plot (Figure 3b) indicates that the percentage of Al in the dispersion solution is correlated to the current, while the percentage in the catholyte is correlated to the duration (they are placed close in the weighted plot). In addition, the weighted plot showed that the difference between the percentage of Al in the dispersion solution and the catholyte was linked to the second component as they had similar values related to the first component but were placed on each side of the x-axis. Thus, mainly L:S, but also the acid concentration, influences the Al distribution as these two variables have the largest influence on the second component. In the experiments where the dispersion solution contained +80% P, about 30% Al mass was also found in the dispersion solution. If considered needed, the weighted plot suggests that a better separation of P and Al in the dispersion solution could be based on the optimization of L:S and acid concentration. Since the Al(+) percentage is on the opposite side of the x-axis to the acid concentration and L:S ratio (Figure 3a), these are negatively correlated, i.e., it suggests that the higher the L:S and the acid concentration, the lower the Al(+) percentage. However, since the Al(+) is close to the x-axis, the effect may be limited.

## 4. Conclusions

Chemometrics modeling was successfully applied to provide insights into the 2C-ED process for simultaneous P extraction and separation of heavy metals from SSA. A new series of ED experiments enabled modeling the process for a specific SSA to explore the influence of the experimental variables. The order of the variables influencing 2C-ED was found through VIP plots to be: current > duration > L:S ratio > stirring velocity > weak acid as dispersion solution. The variables mutually influence each other during the process and the developed model enables investigation of the extraction and separation processes using different combinations of variables. For example, contour plots illustrating different extraction strategies showed that the same applied current was used more efficiently at an L:S ratio of 7 rather than L:S 14. If upscaled, more P could be removed per unit of time in the thickest suspension supporting less voluminous 2C-ED plants. Thus, it was found that the L:S ratio strongly influenced the current efficiency of the process. The chemometric model was shown to be an effective tool for optimizing the 2C-ED process parameters. The knowledge obtained on the process parameters can, accordingly, be used for optimizing the set-up/plant itself, and, thus, chemometric modeling is a valuable tool when designing, for example, an improved laboratory set-up or a pilot scale plant. When first generated, the model enables ready testing and optimization of different combinations of variables within the investigated space without the need for extensive experimental laboratory programs.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/su151813953/s1>: Section S1: Literature data and PLS model, Section S2: Experimental results, Section S3: The screening model, and Section S4: Additional figures related to the extended model. Refs. [12,19–21,25–27] are cited in the supplementary materials.

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