

Recovery of nutrients from digested sludge as struvite with a combination process of acid hydrolysis and Donnan dialysis

Ayla Uysal, Dilara Tuncer, Esengul Kir and Tugba Sardohan Koseoglu

ABSTRACT

In this study, the effects of the combination of acid hydrolysis and Donnan dialysis on the high-quality struvite production from digested sewage sludge were examined. The Box–Behnken design was applied in the hydrolysis using oxalic acid for the optimization of the conditions that affect the nutrients and metal release from digested sludge. An optimal condition was obtained at oxalic acid 0.5 M, acid/sludge ratio (mL/g) 10/1, and reaction time 60 min. The separation of the metals from hydrolyzed sludge liquid was carried out with the Donnan dialysis using a Nafion 117 cation exchange membrane. At the end of the 4 hours of operating time, the recovery values for Zn, K, Na, Mg, Fe, and Al were obtained as 67.9%, 62.1%, 57.6%, 39.4%, 5.3%, and 2.5%, respectively. The produced struvite meets the legal limits for fertilizer use in terms of Cd, Cu, Ni, Pb, Zn, Hg, and Cr content specified by Turkish regulations. A high Ca/Mg molar ratio and the presence of K, Na, and Al affected the efficiency of struvite crystallization. The use of oxalic acid resulted in low Ca release, and the metal ions that affect struvite purity were eliminated using Donnan dialysis.

Key words | Box–Behnken design, Donnan dialysis, fertilizer quality, metal separation, nutrients recovery, oxalic acid hydrolysis

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INTRODUCTION

Global phosphorus resources have been rapidly depleted (Gilbert 2009; Wang *et al.* 2016). Natural phosphorus deposits will supply the needed amounts only for 30 to 60 years (Cieslik & Konieczka 2017; Ye *et al.* 2017). Some studies report that only 18% of phosphorus deposits will be consumed by the year 2050. On the other hand, some studies claim that the quality of phosphorus ores will decrease to an unsatisfactory level by the year 2200. The quality of the available phosphorus deposits is already decreasing; only 20% of the existing phosphorus can be used in agriculture. Other phosphorus deposits contain high levels of heavy metals, particularly cadmium and radioactive elements such as uranium or radon (Cieslik & Konieczka 2017). Therefore, recovery and recycling of phosphorus is critical for a sustainable world (Kim *et al.* 2015). Phosphate rock, the main P resource in the world, is non-renewable. Phosphorus can also be recycled from phosphorus-rich residues, such as meat and bone meal, municipal sewage sludge, phosphorus-rich ashes, and

agricultural residues (Tan & Lagerkvist 2011). Sewage sludge is a very promising phosphorus resource, because it contains the second-highest amount of phosphorus found world-wide (Cieslik & Konieczka 2017). In a second-level biochemical sewage treatment system, more than 90% phosphorus and parts of the nitrogen in the influent will be transferred into the sludge (Balmer 2004); thus, phosphorus and nitrogen usually account for up to 4% and 9% of the dry sludge (Bi *et al.* 2014). Even though waste sludge has a high phosphorus content, it cannot be directly applied to agricultural land as fertilizer because it is usually contaminated with pathogens, heavy metals, or other pollutants (Babel & Dacera 2006). To find an efficient way to release phosphorus and nitrogen from sewage sludge is the first step for phosphorus and nitrogen recovery (Bi *et al.* 2014). Release of phosphorus is most often obtained from the sludge through chemical extraction using mineral or organic acids. However, extraction using acids results in leaching of metals (Tan & Lagerkvist 2011; Cieslik &

Konieczka 2017). Phosphorus released from sludge by extraction is often recovered through crystallization as hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$ or struvite (MgNH_4PO_4) (Doyle & Parsons 2002; Kim et al. 2015). Phosphorus recovery by struvite crystallization is affected by the presence of metals, such as Ca, K, Na, and Al (Pastor et al. 2008). Heavy metals may also affect the quality of recovered phosphorus as clean fertilizer. Sludge may simultaneously release heavy metals at a low pH level. In this case, the recovered product may still be contaminated with heavy metals. Many technologies, such as ion exchange and nanofiltration, are used to remove heavy metals from phosphorus-rich leachate to recover phosphate easily (Ye et al. 2017). However, there have been only a few investigations that focus on the separation of released phosphorus and metals from the acidic hydrolysis supernatant of sewage sludge (Güney et al. 2008; Blöcher et al. 2012). Donnan dialysis has been successfully used for recovery of valuable ions or removal of undesirable ions from a variety of dilute waste streams (Wang et al. 2010). Donnan dialysis, unlike the classical dialysis technique, is a membrane process used to exchange ions between two solutions, the feed and receiver solutions, separated by an ion exchange membrane. The driving force is the difference in the electrochemical potential on the two sides of the membrane. Thus, fluxes of the two solutions moving through the membrane appear in opposite directions (Şahin et al. 2009; Kir et al. 2011). The main advantage of Donnan dialysis is that it is economical, easy to apply, and, especially, energy-saving (Şahin et al. 2009). However, applications of Donnan dialysis to recover ions from slurries or waste streams with high solids content are extremely limited.

This study had four goals. The first goal was to investigate the characteristics of digested sludge hydrolysis by inorganic acids and organic acids at different molar concentrations. These characteristics would be evaluated in terms of the release of Ca, Mg, Na, P, Al, Fe, Zn, Cr, Pb, Cu, and Ni. The second goal was to investigate the optimization of conditions for release of high phosphate and N and low Ca, Mg, Na, K, Al, Fe, and Zn from digested sludge using oxalic acid by the Box–Behnken design. The third goal was to investigate the selective separation of released phosphate, N, Na, K, Mg, Al, Fe, and Zn in the hydrolyzed liquid obtained under optimal conditions using Donnan dialysis. The fourth goal was to examine recovery of nutrients by struvite crystallization from the liquid separated from metal ions. The struvite produced was analyzed by an X-ray diffractometer (XRD) and energy-dispersive X-ray (EDX) spectroscopy.

MATERIALS AND METHODS

Sludge sampling and sample pre-treatment

The anaerobically digested sewage sludge used in this study was taken from a wastewater treatment plant with an enhanced biological phosphorus removal process, located in Antalya, Turkey. The sludge samples were oven dried at $103 \pm 2^\circ\text{C}$ for 42 h, then finely ground and sieved to 1-mm mesh size. These samples were used for metal and nutrient measurements, and hydrolysis experiments.

Characteristics of anaerobically digested sewage sludge

The main characteristics of the anaerobically digested sewage sludge were as follows (Uysal et al. 2016): total solid (TS), 3%; total volatile solid (TVS), 2.90%; total chemical oxygen demand (TCOD), $32,800 \pm 1,555.63$ mg/L; soluble chemical oxygen demand (SCOD), 823 ± 26.87 mg/L; total nitrogen (TN), 4.19%; total phosphorus (TP), 2.00%; and pH, 8.03. Table 1 shows the mean concentrations of the inorganic components in digested sludge as measured during the duplicate analysis (Uysal et al. 2016). The digested sludge contains a high concentration of Ca, Mg, K, Na, Al, Fe, Zn, Cu, Pb, and Ni. However, the digested sludge had low concentrations of Cr. Cd and Hg concentrations were below the detection limit.

Table 1 | Elemental composition of the digested sludge

Element	Concentration (mg/kg)
Ca	$83,380 \pm 112.1^a$
Mg	$10,620 \pm 18.0$
K	$11,560 \pm 19.7$
Na	$11,280 \pm 21.2$
Al	$6,831 \pm 10.2$
Fe	$6,140 \pm 11.2$
Zn	$10,960 \pm 30.5$
Cu	917 ± 9.35
Cr	70.42 ± 0.16
Pb	487.4 ± 6.28
Ni	363.3 ± 3.48
Cd	b.d. ^b
Hg	b.d.

^aMean \pm SD ($n = 2$).

^bb.d., below detection limit.

Hydrolysis experiments

Hydrolysis was performed using a Biosan MSH-300i magnetic stirrer (250 rpm) at constant room temperature. The hydrolysis was carried out in two stages. Firstly, inorganic acids (HCl, HNO₃, and H₂SO₄) and organic acids (acetic, citric, and oxalic) hydrolysis was performed using solutions of increasing concentration (0.1, 0.5, and 1.0 M) at a liquid (mL) to solid (g) ratio of 10/1 for 1 h. Suitable acid was determined in terms of release of phosphorus and metals. Secondly, the Box–Behnken design was employed to optimize high nutrients and low metals released from digested sludge using the suitable acid concentration determined in the first step hydrolysis.

After reaction time in all hydrolysis tests, the samples were centrifuged at 8,000 rpm for 10 min to precipitate the sludge samples. The hydrolyzed sludge liquid or supernatant was filtered through 0.45- μ m membrane filter, and the concentration of phosphorus and metals in the solution was analyzed.

Box–Behnken experimental design and statistical analysis

Box–Behnken, a spherical and revolving design, was used during the optimization of chemical and physical processes (Dong et al. 2009). The Box–Behnken design was specifically selected because it requires fewer runs than a central composite design in cases with three or four variables. Therefore, selecting the Box–Behnken experimental design in this study allowed the elimination of some additional experiments, as well as time-consuming and exhausting laboratory studies. The optimal conditions for maximizing the nutrient release and minimizing the metal release were determined by a three-factor, three-level Box–Behnken experimental design. The total number of tests required for the three independent variables studied in the hydrolysis process (acid concentration (X_1), liquid/solid ratio (X_2), and reaction time (X_3)) was 15. Experimental levels used for the three factors were coded as -1 , 0 , and 1 . The experimental range and levels of independent variables considered in this study are presented in Table 2.

Analysis of variance (ANOVA) was used to analyze the results with Minitab 16 software (Minitab, Inc., State College, PA, USA). Minitab 16 software was used for regression and graphical analyses of the data. The significance of independent variables and their interactions was tested by ANOVA. It was determined that results with less than 95% confidence

Table 2 | Experimental range and coded levels of the independent variables in hydrolysis tests

Coded levels	Variable ranges		
	Acid concentration (M), X_1	Liquid/solid ratio (mL/g), X_2	Reaction time (min), X_3
Low level (-1)	0.3	5/1	30
Center level (0)	0.5	10/1	60
High level ($+1$)	0.7	15/1	90

interval ($P > 0.05$) were not statistically significant for the model. According to the Minitab 16 software, each of the responses could be fitted by a predictive polynomial quadratic model, as shown in Equation (1):

$$Y = a_0 + a_1x_1 + a_2x_2 + a_3x_3 + a_{12}x_1x_2 + a_{13}x_1x_3 + a_{23}x_2x_3 + a_{11}x_1^2 + a_{22}x_2^2 + a_{33}x_3^2 \quad (1)$$

where Y is release of nutrients or metals (mg/L); x_1 , x_2 , x_3 are coded non-dimensional factors for acid concentration, liquid/solid ratio and reaction time, respectively; a_0 is the constant term; a_1 , a_2 , a_3 are linear effect terms; a_{12} , a_{13} , a_{23} , a_{24} are interaction effect terms; and a_{11} , a_{22} , a_{33} are quadratic terms.

Donnan dialysis experiments

Donnan dialysis experiments were carried out using a laboratory cell consisting of two detachable compartments made of Teflon. The volume of each compartment was 140 mL and the solutions were mixed. Nafion 117 (DuPont) cation exchange membrane samples were treated with distilled water at 40 °C for 1 h, then immersed in 1 M HCl for 1 h, washed with distilled water, and then treated with 1 M NaOH for 1 h. Finally, the membrane discs were immersed in 1 M HCl solution for 24 h to convert the membrane samples to the H⁺ form. The area of the exposed membrane was 23.75 cm².

Donnan dialysis experiments were performed with the hydrolyzed sludge liquid obtained under optimal conditions selected by the Box–Behnken design, with the hydrolyzed sludge liquid (110 mL) placed on the feed side and 1 M HCl (110 mL) placed on the receiver side. Figure 1 provides a schematic diagram of the experimental setup using a combination process of acid hydrolysis and Donnan dialysis. The difference of the electrochemical potential on the opposite sides of the membrane acts as the driving force. Thus,

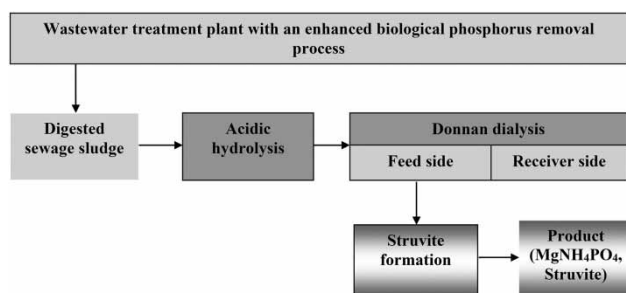


Figure 1 | Schematic diagram of the experimental setup using a combination process of acid hydrolysis and Donnan dialysis.

fluxes of the two counter-ions moving through the membrane appear in opposite directions (Şahin *et al.* 2009). Samples were collected as before at specific time intervals from both the feed and receiver sides of the Donnan cell to analyze soluble orthophosphate ($\text{PO}_4^{3-}\text{-P}$), ammonia nitrogen ($\text{NH}_4^+\text{-N}$), and metal ion compositions.

Metal ions were separated from hydrolyzed sludge liquid using a cation exchange membrane by a Donnan dialysis process. The flux value (J) of metal ions was calculated from the slope of the amount of transported quantity vs. time curves (Tor *et al.* 2004). The metal ion flux was calculated using the following equation:

$$J = \left(\frac{V}{A}\right) \left(\frac{dC}{dt}\right)_{t \rightarrow 0} \quad (2)$$

where V is the volume of receiver phase, A is the effective membrane area, C is the concentration of the metal ions in the receiver solution and t is time.

To compare the recovery of metal ions, the recovery factor (RF) was evaluated for the experimental systems in which the RF for Donnan dialysis process was defined as follows:

$$\text{RF} = \left(1 - \frac{C_0 - C_t}{C_0}\right) \times 100 \quad (3)$$

where C_t is the metal concentration at time t in the receiver phase and C_0 is the initial concentration of metal in the feed phase (Kir *et al.* 2011).

Struvite formation

Hydrolyzed liquid that was separated from metal ions by Donnan dialysis was used for struvite formation. The batch chemical precipitation experiments for struvite formation were conducted in 80 mL volume with continuous stirring with a magnetic stirrer at room temperature (stirring speed

250 rpm). The formation of struvite requires Mg^{2+} , NH_4^+ , and PO_4^{3-} with an ideal molar ratio 1:1:1. In this study, the release of molar concentration $\text{PO}_4\text{-P}$ was greater than that of $\text{NH}_4\text{-N}$ (Table 3) during acidic hydrolysis with oxalic acid. Thus, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and NH_4Cl were used as additional sources of Mg^{2+} and NH_4^+ to simultaneously recover $\text{PO}_4\text{-P}$ and $\text{NH}_4\text{-N}$.

The pH value of the sample was adjusted to the desired level with NaOH (10% and 5%), and the pH was maintained at the desired level. Samples were stirred for 30 minutes and then held for 1 h to allow the precipitate of solid matter to form. Then, the contents of the beaker were filtered through a coarse filter. Solid matter left on the coarse filter was dried by holding at room temperature for 48 hours.

Analytical procedure

TS, TVS, and TN were analyzed by the procedure described in the standard methods (APHA/AWWA/WEF 2005). TCOD and SCOD were determined by the Hach reactor digestion method. $\text{PO}_4^{3-}\text{-P}$ and $\text{NH}_4^+\text{-N}$ were determined using the Hach ascorbic acid method and the Hach Nessler method, respectively. To analyze total metal and TP contents, 1.0 g of sludge sample was weighed and microwave digested using HNO_3 , HCl, and HF. Ca, Mg, K, Na, Al, Fe, Zn, Cu, Cr, Pb, Ni, Cd, and Hg were measured using inductively coupled plasma optical emission spectrometry (Perkin Elmer, DV2100) after acidic microwave digestion. SCOD, $\text{PO}_4^{3-}\text{-P}$, and metal contents were determined by filtering the sample through 0.45- μm membrane filters. The pH values of digested sludge were measured using 1:5 water extraction, mechanically stirred for 3 h, and subsequent determination using a Hanna HI 221 pH meter.

The crystal structure of the dry precipitate was determined using an XRD (Philips, X'Pert Pro). In addition, the dry precipitate was analyzed to determine the composition using an EDX analyzer. To determine metal and TP contents of the dry precipitate, microwave digestion was applied by the addition of HNO_3 and HCl to 0.1 g of solid sample in pressure-resistant Teflon tubes (Uysal *et al.* 2010).

RESULTS AND DISCUSSION

Effects of inorganic acids and organic acids on release of phosphorus and metals from digested sludge by hydrolysis

The results of the released phosphorus and metals in digested sludge using inorganic and organic acids were

Table 3 | Release of nutrients and metals from digested sludge using oxalic acid by Box–Behnken design

Test no.	X ₁ (oxalic acid, M)	X ₂ (liquid/solid ratio, mL/g)	X ₃ (reaction time, min)	PO ₄ -P ^a release (mg/L)	NH ₄ -N release (mg/L)	Ca release (mg/L)	Mg release (mg/L)	Na release (mg/L)	K release (mg/L)	Al release (mg/L)	Fe release (mg/L)	Zn release (mg/L)
1	0.3	5	60	1,841.67	547.50	13.56	858.60	924.70	836.40	172.90	156.10	16.04
2	0.7	5	60	2,355.56	750.00	7.64	1,011.00	798.80	823.80	375.80	557.90	1.83
3	0.3	15	60	936.57	251.25	11.03	446.10	360.40	379.50	159.60	244.10	30.41
4	0.7	15	60	884.03	271.25	9.60	409.80	316.30	54.73	170.20	248.20	32.82
5	0.3	10	30	1,287.50	348.75	5.63	598.00	518.60	533.40	184.20	279.20	27.83
6	0.7	10	30	1,291.67	355.83	13.12	612.60	488.20	71.80	238.70	343.60	23.81
7	0.3	10	90	1,387.50	318.75	4.66	645.60	518.60	538.90	216.90	324.80	38.18
8	0.7	10	90	1,450.00	324.17	13.85	635.40	475.90	69.06	275.20	378.40	28.01
9	0.5	5	30	2,750.00	647.50	4.90	1,072.00	1,010.00	1,026.00	352.30	551.80	21.91
10	0.5	15	30	891.67	246.25	16.26	417.30	315.30	145.50	151.10	225.80	34.12
11	0.5	5	90	2,950.00	807.50	4.50	1,024.00	916.50	930.40	359.70	556.60	7.67
12	0.5	15	90	902.78	255.00	22.09	447.10	324.10	195.50	175.10	255.10	42.73
13	0.5	10	60	1,494.44	392.00	9.19	637.60	503.50	285.90	249.60	361.40	21.55
14	0.5	10	60	1,411.11	358.33	12.22	642.70	491.50	323.20	249.40	373.60	30.87
15	0.5	10	60	1,441.67	360.00	12.13	613.10	482.40	364.10	238.40	356.10	21.66

^aThe release of nutrients and metals refers to the mean concentrations obtained from the duplicate analyses.

partially presented in the authors' previous study (Uysal *et al.* 2016). In all hydrolysis tests using inorganic and organic acids, Ca, Mg, Na, K, Al, Fe, and Zn were released together with the phosphorus, whereas Cr, Pb, Cu, and Ni had a lower release. For phosphorus recovery as struvite, Ca release was unfavorable; because calcium phosphate can be crystallized under certain conditions, it affects the purity of the struvite (Wang *et al.* 2016). Hwang & Choi (1998) and Le Corre *et al.* (2005) indicated that the molar ratio of Ca:Mg should be below 1 for effective struvite formation. The author's previous study showed that HCl, HNO₃, and citric and acetic acid applications were efficient for releasing Ca. The lowest Ca release was accomplished using oxalic acid (Uysal *et al.* 2016). Therefore, we chose oxalic acid hydrolysis for phosphorus release. Results for optimization conditions for release of nutrients and metals using oxalic acid are given in this study.

Optimization of conditions for release of high phosphate, nitrogen and low metals using oxalic acid by Box–Behnken design

Box–Behnken design was employed to optimize high PO₄-P, NH₄-N, and low metals release from the digested sludge

using oxalic acid by hydrolysis. Table 3 shows experimental conditions and release of PO₄-P, NH₄-N and metals from digested sludge using three factors (acid concentration, liquid/solid ratio, and reaction time) in Box–Behnken design. The release of Cr, Pb, Cu, and Ni was not determined, as they were already present in trace concentrations in the hydrolyzed sludge liquid (Uysal *et al.* 2016).

Release of both PO₄-P and NH₄-N significantly increased in cases when liquid/solid ratio was below the central point (Table 3). However, acid concentration and reaction time did not appear to have significant effect on release of both PO₄-P and NH₄-N under any test condition. Increasing acid concentration would cause a significant increase in release of Al and Fe. Decreasing liquid/sludge ratio would cause a significant increase in release of K, Al, Fe, Na, and Mg. Consequently, Table 3 shows that decreasing the liquid/solid ratio was efficient for the release of PO₄-P, NH₄-N, and metals (K, Al, Fe, Na, and Mg). For nutrient recovery, central point conditions (test no. 13–15) were preferable for the low release efficiency for metals, and for improved metal separation from hydrolyzed sludge liquid using Donnan dialysis.

The model adequacy was checked by an F -test and the determination coefficient (R^2). The F values of the models for release of $\text{PO}_4\text{-P}$ and $\text{NH}_4\text{-N}$ were 10.03 and 14.98, respectively; these were much greater than the tabulated F value ($F_{\text{table}} = F_{\alpha, \text{df}_1, (\text{n}-\text{df}+1)} = F_{0.05, 2, 14} = 3.74$) at the 95% significance level. The F values of the models were highly significant in the regression models.

The second-order polynomial model for release of $\text{PO}_4\text{-P}$ and $\text{NH}_4\text{-N}$ (Y) was regressed by considering only the significant terms, shown in Equations (4) and (5):

$$Y_{\text{P}} = 1449.07 - 785.27x_2 + 287.41x_2^2 \quad (4)$$

$$(R^2 = 0.9475, \text{ adjusted } R^2 = 0.8531)$$

$$Y_{\text{N}} = 370.11 - 216.09x_2 + 118.54x_2^2 \quad (5)$$

$$(R^2 = 0.9642, \text{ adjusted } R^2 = 0.8999)$$

As seen in Equations (4) and (5), the first-degree main effect (liquid/solid ratio (x_2)) and the second-degree main effect (x_2^2) on release of $\text{PO}_4\text{-P}$ and $\text{NH}_4\text{-N}$ were the significant model terms. The values of R^2 were greater than 0.94 for both Y_{P} and Y_{N} , suggesting that the regression models were appropriate for simulating the experimental data. Also, the values of adjusted R^2 for Y_{P} and Y_{N} were high, showing a high significance of the models.

The R^2 value was used to determine how well the model fit for the release of metals (Y) (Table 4). The regression models showed statistical significance for the release of all the metals. Except for Fe, both the adjusted R^2 and the R^2 were sufficiently high to support the significance of the models. The linear terms of x_1 (acid concentration) and x_2 (liquid/solid ratio) were significant for Y_{K} , Y_{Al} , and Y_{Fe} . The linear term of x_3 (reaction time) was significant only for Y_{Zn} (data not shown).

The properties of the hydrolyzed sludge obtained at the central point conditions, at which optimum nutrient and metal release occur, are shown in Table 5. Approximately

Table 5 | Properties of the hydrolyzed sludge using oxalic acid obtained from central point conditions by Box-Behnken design

Element	Concentration (mg/kg)
TP	10,350 ± 154.7
Ca	67,770 ± 222.7
Mg	2,902 ± 25.9
K	1,736 ± 27.8
Na	1,705 ± 8.2
Al	5,306 ± 38.70
Fe	4,934 ± 38.4
Zn	800 ± 4.38
Cu	160 ± 0.79
Cr	46.08 ± 0.42
Pb	30.05 ± 1.02
Ni	29.93 ± 0.11

47% of TP was released from the digested sludge by oxalic acid treatment. The digested sludge contains a high concentration of Zn, Cu, Pb, and Ni (Table 1). Those values confirmed that the hydrolyzed sludge produced by oxalic acid treatment was suitable for land application according to the US Environmental Protection Agency (US EPA 2000).

Evaluating the selective separation of released phosphorus and metals from hydrolyzed sludge liquid by Donnan dialysis

In the study of separation of metals from sludge liquid hydrolyzed with H_2SO_4 by Donnan dialysis, HCl was used at two different concentrations (0.1 M and 1 M) in the receiver phase (Uysal et al. 2016). Use of 1 M HCl for 24 hours resulted in an increased transport of the metals to the receiver phase. In addition, when the recovery values were evaluated with respect to time, the recovery was almost constant after 6 hours. Therefore, in this study, separation of metals from hydrolyzed sludge liquid using oxalic acid by Donnan dialysis was carried out using 1 M HCl in the receiver phase for 4 hours of operation time. Hydrolyzed sludge liquid obtained from central point conditions using Box-Behnken design was used in the feed side. The flux values and hydrated radii of the metal ions are presented in Table 6; the fluxes of Na, Mg, and K through the membrane were higher than those for Al, Fe, and Zn.

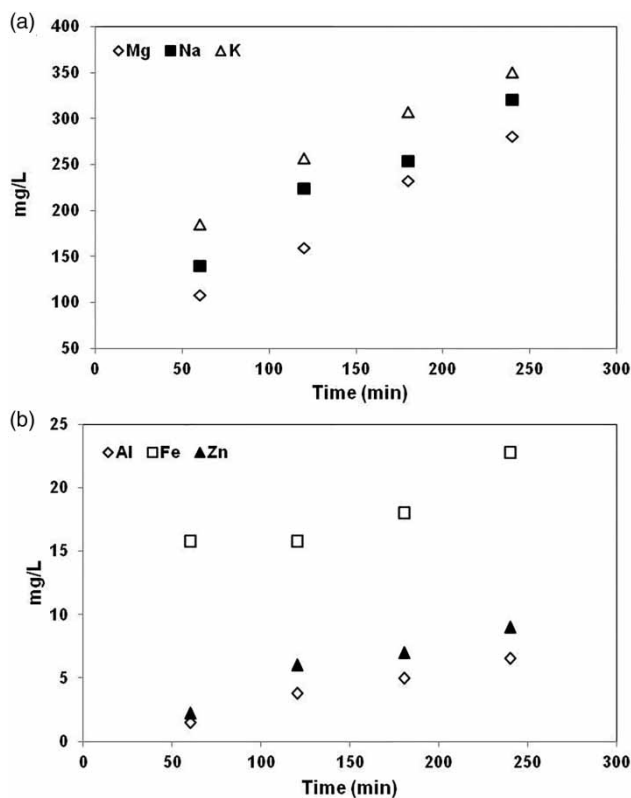
The metal concentrations that were transported to the receiver phase are shown in Figure 2(a) and 2(b). The highest transport was obtained for K (Figure 2(a)). Metal ions of higher

Table 4 | The regression analysis for the model of metal release

Model of metal release (Y)	R^2	Adjusted R^2
Y_{K}	0.9563	0.8778
Y_{Al}	0.9360	0.8209
Y_{Fe}	0.8557	0.5958
Y_{Zn}	0.9343	0.8160
Y_{Na}	0.9879	0.9660
Y_{Mg}	0.9869	0.9633

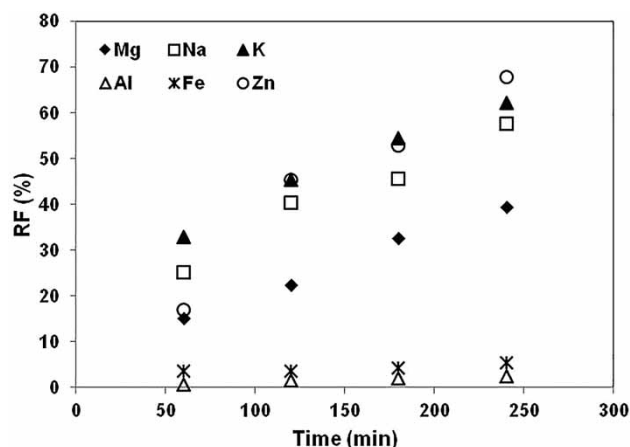
Table 6 | Flux values and hydrated radius of metal ions

Metal ions	$J \times 10^{-9}$ (mol/(cm ² ·s))	Hydrated radius (nm) (Nightingale 1959)
Mg ²⁺	3.11 ± 0.0052	0.428
Na ⁺	3.2 ± 0.0246	0.358
K ⁺	1.8 ± 0.0063	0.331
Al ³⁺	0.078 ± 0.0003	0.475
Fe ³⁺	0.054 ± 0.0028	0.451
Zn ²⁺	0.042 ± 0.0007	0.430

**Figure 2** | Receiver side concentrations for (a) Mg, Na, and K, (b) Al, Fe, and Zn.

valence tend to hydrate more strongly, are bigger, and thus diffuse more slowly (Wang *et al.* 2010). In Donnan dialysis, the transport of ions that have the same valence is influenced by the concentration of feed ions and hydrated ion sizes (Şahin *et al.* 2009). The high transport of K was the result of the low K valence and hydrated radius (Table 6). The transport of Al was low due to its high hydrated radius (Figure 2(b)).

RF values of metal ions in the receiver side are shown in Figure 3. At the end of 4 hours of operation time, the recovery values for Zn, K, Na, Mg, Fe, and Al were obtained as 67.9%, 62.1%, 57.6%, 39.4%, 5.3%, and 2.5%, respectively.

**Figure 3** | RF values of metals in the receiver side.

Further, 9.6% PO₄-P was transported into the receiver side (data not shown). The RF values of K, Na, and Zn were considerably high during the relatively short operation time. Phosphorus recovery by struvite formation is affected by the presence of metals, such as K, Na, Ca, and Al. Phosphorus can precipitate as the metal phosphate by reacting with metals during the struvite formation (Jaffer *et al.* 2002). It was found that a high concentration of Na in the anaerobic effluent of the dairy processing industry affected the formation of struvite (Uysal & Kuru 2013). Thus, the possible negative effects of K, Na and Zn on the recovery of the remaining phosphate in the feed phase were eliminated to a large extent.

Properties of struvite produced from liquid separated from metal ions using Donnan dialysis

Hydrolyzed liquid that was separated from metal ions using Donnan dialysis was used for struvite formation. Struvite formation is more favorable when the ratio of Mg:P is 1:2.5 (Wang *et al.* 2016), and the molar ratio of P:N has to be at least 1:1 (Cieslik & Konieczka 2017). In this study, Mg²⁺:NH₄⁺:PO₄³⁻ was arranged at 1.5:1:1, and pH was held at 9.0. Then, struvite crystals were formed. The removal rates of PO₄-P and NH₄-N were 97.6% and 47.3%, respectively.

XRD analysis results of the dry precipitate matched with the database model given for struvite in terms of position and intensity of peaks (data not shown). The chemical properties of the dry precipitate were also analyzed by EDX. In addition to the principal elements of struvite (i.e., P, Mg, N, O), abundant C and Na were detected in the dry precipitate (Figure 4). This indicates the co-precipitation of struvite and some organic

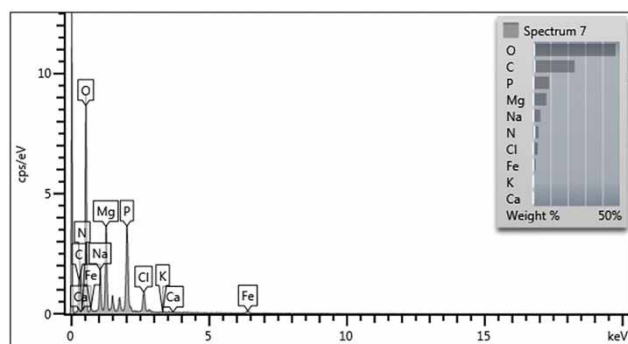


Figure 4 | Chemical composition of the dry precipitate as analyzed via EDX.

compounds present in the hydrolyzed liquid. However, EDX analysis showed a small amount of Ca, K, and Fe.

The produced struvite precipitate had a composition of 3.17% N, 6.84% Mg, and 12.41% P for a molar ratio $Mg^{2+}:NH_4^+:PO_4^{3-}$ of 1.5:1:1 at pH 9.0 (Table 7). However, contents of K, Ca, Al, and Fe were very low. This result showed that the influence of main metal content on the produced struvite purity was minimized by applying Donnan dialysis.

Heavy metals could be a great concern in agronomic applications if the recovered struvite is applied as a fertilizer (Li & Zhao 2003). As shown in Table 8, the concentrations of Cd, Ni, Pb, and Hg in the struvite produced were below detection limits. Although the anaerobically digested sewage sludge had a considerably high Zn content ($10,960 \pm 30.5$ in Table 1), the Zn-value of the produced struvite was below the legal limit value.

Table 7 | Characteristics of produced struvite precipitate

N (%)	Mg (%)	P (%)	K (%)	Ca (%)	Na (%)	Al (%)	Fe (%)
3.17	6.84	12.41	0.846	0.030	3.3	1.00	1.30

Table 8 | Allowable limits for heavy metals in fertilizer (Turkey Organic Fertilizer Regulations 2014) and results obtained for produced struvite in this study

Heavy metal (mg/kg)	Produced struvite	Legal limit values according to Turkey regulations
Cd	b.d.	3
Cu	$0.72 \pm 0,01$	450
Ni	b.d.	120
Pb	b.d.	150
Zn	285.6 ± 1.11	1,100
Hg	b.d.	5
Cr	13.35 ± 0.05	350

b.d., below detection limit.

CONCLUSIONS

Oxalic acid is the recommended acid for digested sludge hydrolysis for low Ca release and high nutrient release. Low Ca content is desirable for appropriate formation of struvite. In addition to this, the other components that affect the purity of struvite – namely, K, Na, Al, Fe, and Zn – were found at high concentrations in the hydrolyzed sludge liquid. Selective separation of metal ions from the hydrolyzed sludge liquid can be achieved by Donnan dialysis. At the end of 4 hours operating time, the recovery values for Zn, K, Na, Mg, Fe, and Al were obtained as 67.9%, 62.1%, 57.6%, 39.4%, 5.3%, and 2.5%, respectively. The valences, the hydrated radii, and the concentrations of metals in the feed phase were effective for the recovery. The EDX analysis of the struvite obtained from the nutrient-rich liquid separated from the metal ions revealed its low Fe, Ca, and K content. The fertilizer quality of the produced struvite was in agreement with the relevant regulations in terms of Cd, Cu, Ni, Pb, Zn, Hg, and Cr contents. Finally, it can be concluded that the combination process of oxalic acid hydrolysis and Donnan dialysis reduces the interfering effects of metal ions on the struvite produced from digested sludge. The significant advantages of Donnan dialysis compared to other ion exchange membrane processes are cost-effectiveness and energy-saving. Donnan dialysis can be used in further practices, such as for phosphorus-rich ashes and wastewater, to separate phosphorus from metals to obtain a fertilizer complying with the regulations. Future studies are planned to examine the use of electrodialysis to separate phosphorus from metals. Electrodialysis may allow a much higher flux and a better separation of metal ions.

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