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OPTIMIZATION OF ALKALINE–THERMAL HYDROLYSIS TO OBTAIN STRUVITE FROM DIGESTED SLUDGE USING A BOX–BEHNKEN DESIGN: SOLUBILIZATION OF NUTRIENTS AND METALS

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Keywords

Alkaline-Thermal Hydrolysis, Hydrolyzed Sludge, Nutrients Recovery, Solubilizaton, Struvite.

Abstract

In this study, we investigated ways by which to optimize metals and nutrients solubilization from sewage sludge using alkaline–thermal hydrolysis and the Box–Behnken design. We also examined through struvite crystallization the recovery of solubilized nutrients from hydrolyzed liquid and determined the effect of NaOH concentration, the liquid/solid ratio, and temperature on the hydrolysis process. Nutrients solubilization was positively affected by decreasing liquid/sludge ratio and increasing NaOH concentration. Ca, Al, and Zn solubilization increased with increasing temperature. The optimum condition for solubilization of nutrients and metals was 0.7 M NaOH and a 5/1 mL/g liquid/solid ratio at 35 °C. EDS analyses of hydrolyzed sludge obtained under optimum conditions showed that the mass percentage of C, P, Fe, Al, and K decreased compared to that of the digested sludge. Under optimum conditions, the removal efficiencies of NH_4^+ and PO_4^{3-} from hydrolyzed liquid by struvite precipitation were 57.43 and 79.22% at a N:Mg:P molar ratio of 1:1:1, and 73.31 and 99.02% at a N:Mg:P molar ratio of 1:1.5:1, respectively. XRD analyses of the dry precipitate showed hazenite in addition to struvite formation at a molar ratio of N:Mg:P of 1:1:1.

BOX–BEHNKEN DİZAYNI KULLANILARAK ÇÜRÜTÜLMÜŞ ÇAMURDAN STRÜVİT ELDE ETMEK İÇIN ALKALİ–TERMAL HİDROLİZİN OPTİMİZASYONU: NÜTRİENTLERİN VE METALLERIN ÇÖZÜNDÜRÜLMESİ

Anahtar Kelimeler

Alkali–Termal Hidroliz, Hidrolize Edilmiş Çamur, Nütrient Geri Kazanımı, Çözündürme, Strüvit.

Öz

Bu çalışmada, alkali–termal hidroliz ve Box–Behnken dizaynı kullanılarak arıtma çamurundan metallerin ve nütrientlerin çözündürülmesinin optimizasyonu araştırılmıştır. Çözündürülmüş nütrientlerin, hidroliz sıvısından geri kazanımı da strüvit kristalizasyonu ile araştırılmış ve hidroliz prosesi üzerine NaOH konsantrasyonu, sıvı/katı oranı ve sıcaklığın etkileri belirlenmiştir. Nütrientlerin çözündürülmesi, azalan sıvı/katı oranı ve artan NaOH konsantrasyonu ile pozitif olarak etkilenmiştir. Ca, Al ve Zn çözündürülmesi sıcaklık artışı ile artmıştır. Nütrientlerin ve metallerin çözündürülmesi için optimum koşullar 0,7 M NaOH, 5/1 mL/g sıvı/katı oranı ve 35 °C'de olmuştur. Optimum koşullar altında elde edilen hidrolize edilmiş çamurun EDS analiz sonuçları, C, P, Fe, Al ve K kütle yüzde değerlerinin çürütülmüş çamurunkine kıyasla azaldığını göstermiştir. Optimum koşullar altında, strüvit çöktürmesi ile hidroliz sıvısından NH_4^+ ve PO_4^{3-} giderim verimleri sırasıyla N:Mg:P molar oranı 1:1:1 iken %57,43 ve %79,22 ve N:Mg:P molar oranı 1:1.5:1 iken %73,31 ve %99.02 olmuştur. Kuru çökeltinin XRD analizleri, N:Mg:P molar oranı 1:1:1 iken strüvit oluşumuna ek olarak hazenit oluşumunu da göstermiştir.

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1. Introduction

Currently, producing chemical fertilizers industrially firmly relies on non-renewable sources of phosphorus (P), like natural deposits of phosphate minerals like apatite rock. A crucial research topic to guarantee the future of global food security requires, instead, an evaluation of renewable resource alternatives to produce fertilizer (Barca et al., 2019). Waste activated sludge contains a significant amount of nutrients, especially nitrogen and phosphorus (Alhraishawi and Aslan, 2022).

One of the most significant issues in wastewater treatment is dealing with waste activated sludge, a rich source of P produced by the action of P-accumulating organisms. Given the expected future depletion of P resources, its recovery from sewage sludge is one very encouraging alternative to eliminate sludge-associated problems (Semerci et al., 2021). Using a chemical wash is the most widespread method used to extract P from waste sludge because it is an inexpensive and simple process (Donatello and Cheeseman, 2013; Meng et al., 2019). Leaching exists when a liquid solution containing a waste and chemicals (acids or bases) flows through the wastes (Sayılgan and Karacan, 2019). Acidic and alkaline solutions can be used to leach P from waste sludge. The potential advantages of both of these washing processes are that they use less energy and produce phosphoric acid and phosphates that can be converted into products with a higher commercial return. These include struvite ($MgNH_4PO_4{\bullet}6H_2O$) and hydroxyapatites or calcium phosphates. However, as a result of the leaching process, the leachate includes elements – predominantly Al, Fe and Ca – and heavy metals alongside P, and recovering P from this leachate is a critical issue (Meng et al., 2019).

Thus, the leaching process must use additional process to remove P from the extracted pollutants, by means of solvent extraction (Donatello and Cheeseman, 2013), sequential precipitation (Takahashi et al., 2001), sulfide precipitation (Franz, 2007), ion exchange membrane processes (Uysal et al., 2017), and chemical precipitation of P.

Directly dissolving it in an alkaline solution is an alternative to dissolving P in acid and then separating the dissolved P from the dissolved metals where most metals solubilized in the sludge liquid. It is also possible to directly extract P using sodium hydroxide (NaOH), but only at an efficiency of 40% (Meng et al., 2019). To mitigate this problem, a combined alkaline-thermal hydrolysis is used, which is considered superior to traditional alkaline hydrolysis (Kim et al., 2015; Takahaski et al., 2015). The combination of chemicals and thermal treatment seems to be more favorable than just thermal treatment (Suarez-Iglesias et al., 2017). While there has been widespread study of the use of alkalis to dissolve sludge, they have largely concentrated on dissolving easily biodegradable carbon involving, soluble chemical oxygen demand (SCOD). By contrast, very few have studied the solubility of P (Tolofari et al., 2020; Zin et al., 2021). In addition, studies are limited on P, N, and metal releases from sewage sludge using alkaline–thermal hydrolysis (Semerci et al., 2021). The conditions affecting hydrolysis must be optimized for nutrients recovery from sewage sludge in the form of struvite.

In the present study, we evaluated the effects of NaOH concentration, liquid/solid (L/S) ratio, and temperature on the hydrolysis of digested sludge using the Box–Behnken design. Under our test conditions, release of maximum nutrients and minimum metals were determined. The chemical composition and morphology of the hydrolyzed digested sludge were compared to the digested sludge. P and N from the hydrolyzed liquid obtained under optimum conditions were recovered using struvite crystallization. The precipitate obtained was analyzed.

2.1. Material and Method

2.1. Sludge Sample and Preparation

Anaerobic sludge digester effluent from a municipal wastewater treatment plant based in Antalya, Turkey, using the anaerobic/anoxic/aerobic method (A^2/O) provided the digested sewage sludge samples for this study. After oven drying at a temperature of 103 ± 2 °C for 42 hours, samples were powdered and sieved to a size of 1 mm or less. Subsequently, the sieved samples were stored in plastic bags at room temperature and sealed until the metals, nutrients measurements, and hydrolysis experiments were performed. Table 1 lists the basic attributes of the digested sludge samples used.

Table 1. Basic characteristics of digested sludge samples used in this study

Parameter	**Value**[a]
pH	7.64 ± 0.2
TS (g/L)	36.45 ± 3.46
TVS (g/L)	25.35 ± 3.04
TCOD (g/L)	51.47 ± 3.49
SCOD (g/L)	1.29 ± 0.05
TN (mg/g)	41.9 ± 1.2
TP (mg/g)	24.75 ± 0.16
Total Metals (mg/g)	
Ca	17.47 ± 0.13
Mg	1.79 ± 0.03
K	4.85 ± 0.04
Na	0.66 ± 0.009
Al	4.83 ± 0.06
Fe	6.19 ± 0.08
Zn	1.59 ± 0.01
Cu	0.12 ± 0.002
Cr	0.04 ± 0.001
Pb	0.014 ± 0.001
Ni	0.02 ± 0.00
Cd	b.d.[b]
Hg	b.d.

[a]data: mean ± standard deviation (n = 2); [b]b.d.: below detection limit.

2.2. Alkaline–Thermal Hydrolysis

In alkaline pretreatment, NaOH is most preferred used because of its high solubilization rate with relatively low dosages (de Sousa et al., 2021). Thus, we used NaOH for alkali hydrolysis in the present study.

In our preliminary study (Uysal et al., 2019), the effects of reaction time, temperature, and L/S ratio factors on the hydrolysis of sewage sludge were investigated by maintaining a constant concentration of NaOH (0.5 M). We observed that the effect of reaction time on release of P is insignificant, but that P release was positively correlated with an increase in temperature and a decrease in the L/S ratio; however, we also realized that Fe, Ca, and Zn releases increased with an increase in temperature. The results obtained within the scope of the preliminary study (Uysal et al., 2019) indicated that it was necessary to investigate the effects of NaOH concentration and a low L/S ratio on P release. Because metal releases increased in parallel with the increase in temperature, we planned to work within a lower temperature range in the present study.

Alkaline–thermal hydrolysis was conducted using a magnetic stirrer with hot plate at 250 rpm. Optimization of low metals and high nutrients releases from digested sludge using alkaline–thermal hydrolysis was performed using the Box–Behnken design. We determined the effects of the parameters, such as NaOH concentration (M), L/S ratio (mL/g), and temperature (°C), on the solubilization of metals and nutrients from digested sludge using alkaline–thermal hydrolysis and the Box–Behnken design.

After hydrolysis, the hydrolyzed samples were centrifuged at 9000 rpm for 20 minutes to separate the solid and liquid fractions. Hydrolyzed sludge obtained under optimum experimental conditions was oven-dried overnight at 103 °C, after which the dried hydrolyzed sludge samples were ground.

2.2.1. Box–Behnken Experimental Design and Statistical Analysis

A Box–Behnken statistical experimental design was chosen to be the most suitable method to optimize the chemical and physical processes (Dong et al., 2009). The Box–Behnken design requires fewer iterations compared to central composite designs. As a result, the Box–Behnken design reduced the number of experiments required and the time taken compared to the intensive laboratory studies that would otherwise have been required.

Specifically, a three factor, three-level Box–Behnken design was applied to determine the optimal conditions required for maximum nutrients solubilization and minimum metals solubilization using NaOH–thermal hydrolysis. The number of experiments applied for the three factors was 15. The three independent variables were studied at three coded levels as –1, 0, and +1. Table 2 shows the levels and experimental range of the three independent variables considered in this study.

Table 2. Levels and variables examined in alkaline–thermal hydrolysis using Box-Behnken design

Coded Levels	**Variables**		
	NaOH (M), X_1	L/S Ratio (mL/g), X_2	Temperature (°C), X_3
Low Level (−1)	0.3	3/1	35
Center Level (0)	0.5	5/1	50
High Level (+1)	0.7	7/1	65

The data was subjected to regression and graphical analyses using the analysis of variance (ANOVA) component within the Minitab 19 statistical software package (Minitab, Inc., State College, PA, USA) to test for the significance of independent variables and how they interacted with each other. In this study, model results with a 95% confidence level were considered statistically significant. The main effects and interaction effects of the variables were predicted with quadratic polynomial model shown below in Eq. (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 solubilization of metals or nutrients (mg/L); x_1, x_2, x_3 are coded independent variables; a_0 is constant coefficient; a_1, a_2, a_3 are linear coefficients; a_{12}, a_{13}, a_{23}, a_{24} are interaction coefficients; and a_{11}, a_{22}, a_{33} are quadratic coefficients.

2.3. Struvite Formation from the Hydrolyzed Sludge Liquid

Hydrolyzed liquid obtained optimum test conditions was used in struvite crystallization experiments. For struvite crystallization, batch chemical precipitation experiments were carried out in a volume of 45 mL with a magnetic stirrer. The formation of struvite needs NH_4^+, PO_4^{3-}, and Mg^{2+} with an ideal molar ratio 1:1:1. Thus, H_3PO_4 and $MgCl_2.6H_2O$ were used as additional reagents of PO_4^{3-} and Mg^{2+} to simultaneously recover NH_4^+ and PO_4^{3-} (Zin et al., 2021).

20% NaOH and 1 M hydrochloric acid (HCl) solutions were used to adjust and maintain the sample pH value at the desired level. The precipitation of solid matter from the samples was achieved by stirring for 30 minutes and then leaving for 1 hour. A coarse filter was then used to filter the contents of the beaker. The solid product on the filter was collected and dried at room temperature for 2 days.

2.4. Analytical Procedure

Total nitrogen (TN), total solid (TS), and total volatile solid (TVS) were performed by the procedure identified in the Standard Methods (APHA, 2005). The Hach reactor digestion method was applied to measure of SCOD and total chemical oxygen demand (TCOD). The Hach Nessler method and the Hach ascorbic acid method were used to determine of ammonium ion (NH_4^+) and phosphate ion (PO_4^{3-}), respectively. The process of analyzing the total phosphorus (TP) and total metal contents was to weigh out 1.0 g of the dried digested sludge sample before employing microwave digestion using HCl, nitric acid (HNO_3), and hydrofluoric acid (HF). Following acidic microwave digestion, metals and TP were measured by an inductively coupled plasma optical emission spectrometer (ICP-OES, Perkin Elmer, DV2100). The hydrolyzed liquids were filtered through a 0.45 µm filter before determining the SCOD, PO_4^{3-} and metal content readings. pH value of the digested sludge was determined by a pH meter (Hanna HI 221).

The morphology and the chemical composition of the dried digested sludge and dried hydrolyzed sludge were performed by a scanning electron microscope (SEM, FEI, Quanta FEG 250) combined with an energy-dispersive X-ray spectroscopy (EDS). An X-ray diffraction (XRD, Philips, X'Pert Pro) was applied to determine the crystalline structures in the dry struvite precipitate.

3. Experimental Results

3.1. Effect of the NaOH Concentration, L/S Ratio, and Temperature on Solubilization of Nutrients and Metals in Digested Sludge and Statistical Significance

A Box–Behnken design was used to optimize maximum solubilization of NH_4^+ and PO_4^{3-} and minimum solubilization of metals from the digested sludge with an alkaline–thermal process. Table 3 shows the solubilization of metals and nutrients.

As NaOH concentration increased, PO_4^{3-} and NH_4^+ releases increased. Compared to 0.3 M NaOH, 0.7 M NaOH produced a significantly larger release of P. The largest release of PO_4^{3-} (3936 mg/L) was obtained in test 6 with 0.7 M NaOH and 5/1 L/S ratio at 35 °C. Under these conditions, NH_4^+ release was 1527.36 mg/L. Strong alkaline conditions (pH > 11) favor the hydrolysis of organic P compounds (Li et al., 2013; Bi et al., 2014). The pH of the hydrolyzed liquids at the end of all tests was ~10–13.5 for all except test 1. The largest PO_4^{3-} release was in test 6 at 13.33 pH of the liquid phase after hydrolysis. The largest NH_4^+ release (1880 mg/L) was in test 2 with 0.7 M NaOH and a 3/1 L/S ratio at 50 °C. Under these conditions, the release of PO_4^{3-} was 2727 mg/L (Table 3). As shown in Table 3, Mg release was insignificant. Similarly, Semerci et al. (2021) have reported that Mg leaching is insignificant, most likely from precipitation with P under alkaline conditions. Yu et al. (2017) reported that the concentration of Mg in the hydrolysate by hydrothermal treatment is insufficient compared to PO_4-P and NH_4-N concentrations.

Table 3. Solubilization of metals and nutrients from digested sludge with alkaline–thermal hydrolysis

Test	X_1	X_2	X_3	PO_4^{3-} (mg/L)	NH_4^+ (mg/L)	Mg (mg/L)	Ca (mg/L)	K (mg/L)	Na (mg/L)	Fe (mg/L)	Al (mg/L)	Zn (mg/L)
1	0.3	3/1	50	720	1563.48	<0.1	130.20	1632.00	5072	72.00	2.50	45.70
2	0.7	3/1	50	2727	1880.82	<0.1	101.70	1765.00	10440	103.70	25.30	32.40
3	0.3	7/1	50	1720	1090.05	<0.1	46.40	816.10	4962	25.10	38.40	14.10
4	0.7	7/1	50	1620	1393.20	3.40	109.50	998.90	12150	61.40	188.20	50.80
5	0.3	5/1	35	1224	1201.64	<0.1	74.60	970.20	4658	25.50	7.40	22.50
6	0.7	5/1	35	3936	1527.36	<0.1	65.30	1259.00	11330	61.20	207.70	31.50
7	0.3	5/1	65	1540	1167.45	<0.1	66.10	995.30	4384	33.10	3.00	15.40
8	0.7	5/1	65	2350	1677.00	<0.1	101.20	1187.00	10420	81.20	179.10	65.20
9	0.5	3/1	35	1295	1573.80	<0.1	100.20	1508.00	6121	75.20	6.60	54.00
10	0.5	7/1	35	2310	825.60	<0.1	18.10	780.10	6155	49.90	115.70	21.50
11	0.5	3/1	65	1554	1548.00	<0.1	126.10	1632.00	6215	47.00	6.50	29.70
12	0.5	7/1	65	2552	598.56	<0.1	84.40	922.10	6891	77.50	112.60	40.10
13	0.5	5/1	50	2035	1238.40	<0.1	60.30	1111.00	6137	60.90	21.00	24.40
14	0.5	5/1	50	1835	1180.35	<0.1	58.10	1005.00	5966	55.10	21.20	21.10
15	0.5	5/1	50	2175	1470.60	<0.1	54.50	1074.00	6103	60.00	29.00	21.20

The significance of each coefficient was determined and evaluated using ANOVA (Table 4). Only regression of the significant parameters (P<0.05) was considered in the second-order polynomial model for the solubilization of PO_4^{3-} and NH_4^+. This is shown in Eqs. (2) and (3):

$$Y_{\mathrm{P}} = 2015 + 679x_1 - 527x_1x_2 \tag{2}$$
$$Y_{\mathrm{N}} = 1296.4 + 182x_1 - 332.3x_2 + 221.2x_1^2 \tag{3}$$

As seen in Eq. (2), NaOH concentration (x_1) and the interaction effect (x_1x_2) on the solubilization of PO_4^{3-} were the significant model terms. As seen in Eq. (3), NaOH concentration (x_1) and L/S ratio (x_2) and the second-degree main effect (x_1^2) on the solubilization of NH_4^+ were the significant model terms. The first-degree main effect importance of (x_3) of temperature on release of PO_4^{3-} and NH_4^+ was lower (Eqs. 2 and 3) than that of the other main effects (x_1 and x_2).

The adequacy of the model was checked by determining the coefficient (R^2). The R^2 values of the models for Y_P and Y_N were 0.8372 and 0.9122, respectively (Table 4). The values for R^2 were sufficiently high enough to validate the models.

Table 4. ANOVA for the second-order polynomial models of release of nutrients

Terms (Coded)	Degrees of Freedom	Sum of Squares	Mean Squares	*F*-Value	*P*-Value	Coefficient
Y_P (R^2= 0.8372)						
Model	9	6880594	764510	2.86	0.13	
Constant					0.001	2015
NaOH concentration	1	3684255	3684255	13.76	0.014	679
L/S ratio	1	454105	454105	1.70	0.249	238
Temperature	1	73920	73920	0.28	0.622	-96
NaOH × NaOH	1	251	251	0.00	0.977	8
L/S ratio × L/S ratio	1	39360	39360	1.47	0.279	-327
Temperature × Temperature	1	211350	211350	0.79	0.415	239
NaOH × L/S ratio	1	1109862	1109862	4.15	0.097	-527
NaOH × Temperature	1	904401	904401	3.38	0.125	-476
L/S ratio × Temperature	1	72	72	0.00	0.988	-4
Residual error	5	1338283	267657			
Lack of fit	3	1279883	426628	14.61	0.065	
Pure error	2	58400	29200			
Total	14	8218878				
Y_N (R^2 = 0.9122)						
Model	9	1430954	158995	5.77	0.034	
Constant					0.000	1296.4
NaOH concentration	1	264905	264905	9.62	0.027	182.0
L/S ratio	1	88357	88357	32.08	0.002	-332.3
Temperature	1	2360	2360	0.09	0.782	-17.2
NaOH × NaOH	1	180589	180589	6.56	0.051	221.2
L/S ratio × L/S ratio	1	4710	4710	0.17	0.696	-35.7
Temperature × Temperature	1	56995	56995	2.07	0.210	-124.2
NaOH × L/S ratio	1	50	50	0.00	0.968	-3.5
NaOH × Temperature	1	8448	8448	0.31	0.604	46.0
L/S ratio × Temperature	1	10124	10124	0.37	0.571	-50.3
Residual error	5	137719	27544			
Lack of fit	3	90542	30181	1.28	0.467	
Pure error	2	47177	23589			
Total	14	1568672				

The interactive effects of the variables on PO_4^{3-} release are illustrated in Figs. 1a–c. The release of PO_4^{3-} significantly increased with the increase in NaOH concentration (Fig. 1a). Kim et al. (2015) have similarly reported that an increase in NaOH concentration (0.001, 0.01, 0.1, and 1 N) applied to the waste active sludge positively affects the P release. They reported that the release of TP were 64%, 86% and 90% at 0.02, 0.1 and 1 M NaOH concentrations, respectively. At the L/S ratio below the center point, there was some decrease in PO_4^{3-} release (Fig. 1a). The concentration of NaOH above the center point and the temperature below the center point increased the release of PO_4^{3-} (Fig. 1b). Kim et al. (2015) have reported that the temperature increase (50–80 °C) had an effect on COD, N, and P release at only low NaOH concentrations; however, the effect was not significant at high concentrations. Similarly in the present study, the effect of an increase in temperature on solubilization of PO_4^{3-} was not significant compared to that of an increase in NaOH concentration. The L/S ratio was at the center point, while the PO_4^{3-} release reached the highest value. We observed that the release efficiency decreased to values below and above the central point (Fig. 1c). Similarly, by applying KOH and NaOH alkalis to the sewage sludge, Falayi et al. (2019) found that the release of P increases when the L/S ratio decreases from 0.5 to 0.25%; however, they have noted that P releases decrease at L/S ratios of <0.25%. In the present study, PO_4^{3-} releases decreased at low L/S ratios, which might have been the result of a reduction in mass transfer efficiency because of more solids being available for a fixed quantity of alkali (reagent starvation) (Falayi et al., 2019; Li et al., 2012; Nosrati et al., 2013; Hosseini et al., 2017).

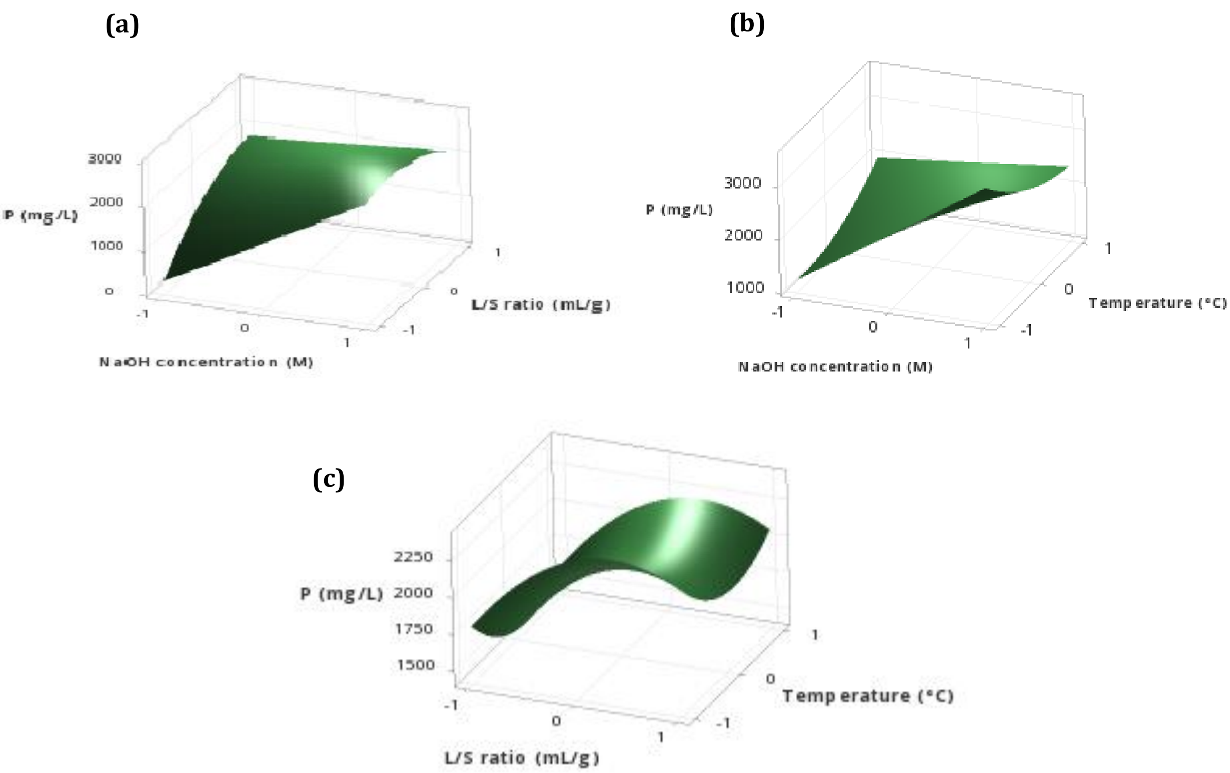


Figure 1. Effects of interaction of **(a)** NaOH concentration × L/S ratio, **(b)** NaOH concentration × temperature, and **(c)** L/S ratio × temperature on P release

The interactive effects of the variables on NH_4^+ release are illustrated in Figs. 2a–c. The release of NH_4^+ increased with the increase in NaOH concentration (Figs. 2a–b). Kim et al. (2015) have similarly reported that TN release increases as the concentration of NaOH applied to the waste active sludge increases. A higher pH caused to more released TN and NH_4^+ because of more releases of nitrogenous organic compounds from the sludge (Xu et al., 2018). As the L/S ratio increased, NH_4^+ releases decreased (Fig. 2a). Although NH_4^+ releases increased significantly with the decreasing L/S ratio, we observed that the effect of temperature changes on NH_4^+ releases was not significant. A slight decrease in NH_4^+ release was observed at temperatures above and below the central point (Fig. 2c).

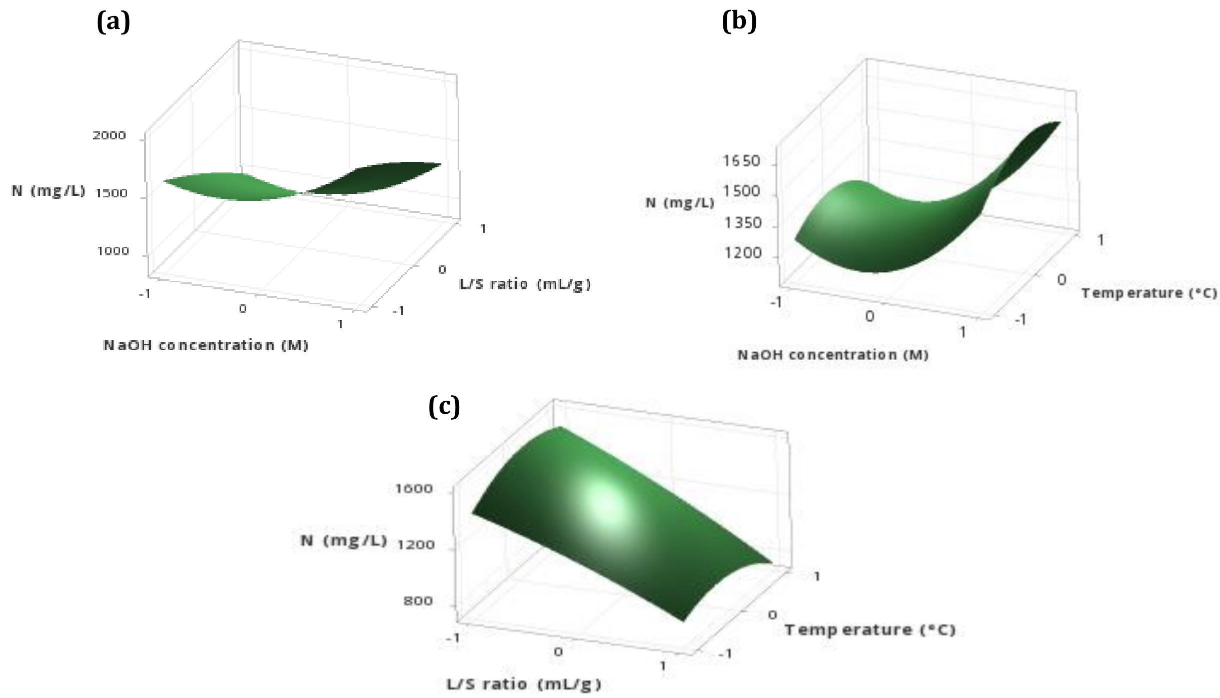


Figure 2. Effects of interaction of **(a)** NaOH concentration × L/S ratio, **(b)** NaOH concentration × temperature, and **(c)** L/S ratio × temperature on N release

Metals and PO_4^{3-} and NH_4^+ were released in all the hydrolysis tests; however, Mg release was comparatively low (Table 3). The R^2 value shows how good a fit the model is in determining the solubilization of metals (Y). The regression models presented were shown to be statistically significant and therefore valid for predicting the solubilization of the following metals: R^2_{Fe} = 0.8044, R^2_K = 0.9826, R^2_{Na} = 0.9933, R^2_{Ca} = 0.9392, R^2_{Al} = 0.9317 and R^2_{Zn} = 0.9074. The second-order polynomial model for metals solubilization in terms of coded factors was regressed by considering only the significant terms, as shown in Eqs. (4) and (9):

$$Y_{\mathrm{Fe}} = 58.67 + 18.98x_1 \quad (4)$$

$$Y_{\mathrm{K}} = 1063.3 + 99.5x_1 - 3377.5x_2 + 173.7x_2^2 \quad (5)$$

$$Y_{\mathrm{Na}} = 6069 + 3158x_1 + 289x_2 + 1720x_1^2 + 455x_1x_2 \quad (6)$$

$$Y_{\mathrm{Ca}} = 57.63 - 24.97x_2 + 14.95x_3 + 16.96x_1^2 + 22.36x_2^2 + 22.90x_1x_2 \quad (7)$$

$$Y_{Al} = 23.7 + 68.6x_1 + 51.8x_2 + 39.4x_1^2 + 36.2x_3^2 \quad (8)$$

$$Y_{Zn} = 22.23 + 10.28x_1 + 12.50x_1x_2 + 10.20x_1x_3 + 10.72x_2x_3 \quad (9)$$

Of the main effects, only NaOH concentration (x_1) was significant on the release of Fe (Eq. 4). NaOH concentration (x_1) and the L/S ratio (x_2) were found to be important first-order main effects on K, Na, Ca, Al, and Zn releases (Eqs. (5–9)). The temperature (x_3) effect was also significant for Ca, Al, and Zn releases (Eqs.(7–9)). The temperature increase positively affected the solubilization of Ca, Al, and Zn. The release of Al increased significantly at an NaOH concentration above the center point; however, the increase in NaOH concentration did not have a significant effect on the Ca release. Similarly, Ali and Kim (2016) have reported that Al and P leaching increases with NaOH concentration, with nearly no increase in Ca concentration. Tolofari et al. (2020) reported that a significant amount of Al was released from the sludge when the pH was greater than 10.

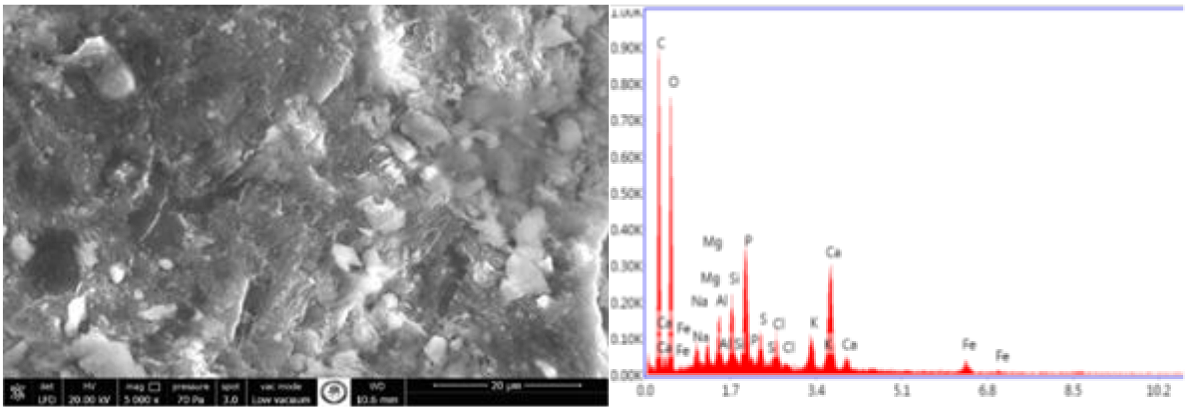
3.2. Optimization of NaOH–Thermal Hydrolysis for Solubilization of Metals and Nutrients from Digested Sludge

PO_4^{3-} releases increased at an NaOH concentration above the center point and a temperature below the center point when the L/S ratio was at the center point. At 0.7 M NaOH and a 5/1 L/S ratio, the largest PO_4^{3-} release was obtained at 35 °C (Table 3). With an increase in temperature, the solubilization of Ca, Al, and Zn also increased. High metal concentrations affect the growth and formation of struvite crystals (Wang et al., 2016). During the test conditions under which there was maximum P release, a temperature below the center point was found to be suitable for metal releases.

3.3. Characterization of Hydrolyzed Sludge Residues Obtained under Optimum Conditions

The digested sludge, and the residual hydrolyzed digested sludge after hydrolysis under optimum conditions were characterized using SEM–EDS to observe the surface morphology and distribution of elements. A comparison of the SEM images of the digested sludge and the hydrolyzed sludge at 5000x magnification is shown in Figs. 3a, b. The morphology of the hydrolyzed digested sludge changed compared to that of the digested sludge. The images show that alkaline–thermal hydrolysis fragmented the aggregates of the digested sludge and that there were several pores on the coarse surface of the hydrolyzed digested sludge. The results of the EDS surface distribution scans showed that the mass percentage of C, P, Fe, Al, and K decreased, which resulted from these elements entering the hydrolyzed sludge liquid, thus decreasing the content in the hydrolyzed sludge residue. Because NaOH was used for hydrolysis, the hydrolyzed sludge contained a significantly higher amount of Na than the digested sludge.

(a)



(b)

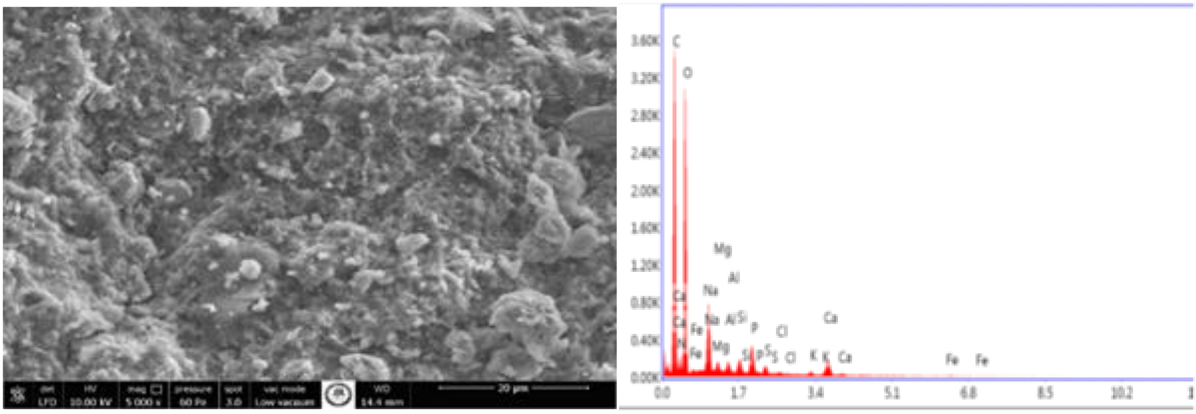


Figure 3. SEM images and EDS analyses of **(a)** digested sludge and **(b)** hydrolyzed digested sludge

3.4. Formation of Struvite from Hydrolyzed Sludge Liquid using Alkaline–Thermal Hydrolysis under Optimum Test Conditions

The hydrolyzed sludge liquid obtained using NaOH–thermal hydrolysis under optimum test conditions was used in the struvite crystallization experiments.

Struvite formation is more suitable when the N:Mg:P molar ratio of is at least 1:1:1 (Cieslik and Konieczka, 2017). In the treatment aimed at P removal and recovery, many studies stressed the importance of applying a Mg/P molar ratio higher than the stoichiometric ratio (Uysal et al., 2010; Siciliano et al., 2020).

In the present study, the N:Mg:P molar ratios of were arranged at 1:1.1 and 1:1.5:1, and pH was held at 9.0. Under these conditions, struvite crystals were formed. The removal efficiencies of NH_4^+ and PO_4^{3-} were 57.43 and 79.22% in the N:Mg:P molar ratio of 1:1:1, and 73.31 and 99.02% in the N:Mg:P molar ratio of 1:1.5:1, respectively. These results indicated that supplementary concentration of Mg is necessary for maximum P removal.

XRD analysis of the dry struvite precipitate showed hazenite ($KNaMg_2(PO_4)_2 \cdot 14H_2O$) formation in the N:Mg:P molar ratio of 1:1:1 in addition to struvite formation (Fig. 4a). Hazenite is a new struvite compound with a structure containing two separate monovalent K and Na cations (Yang et al., 2011). The hazenite "relative" struvite has shown promise as a slow-release fertilizer with highly effective P (Weissengruber et al., 2018). Watson et al. (2020) have reported that hazenite is a new secondary P, K, and Mg fertilizer. Arslanoğlu and Tümen (2021) have reported that potassium struvite and hazenite formed from vinasse and grape marc organic waste using thermal processing.

The dry precipitate obtained in the N:Mg:P molar ratio of 1:1.5:1 matched that of the database model for pure struvite in terms of intensity of peaks and position (Figs. 4b,c).

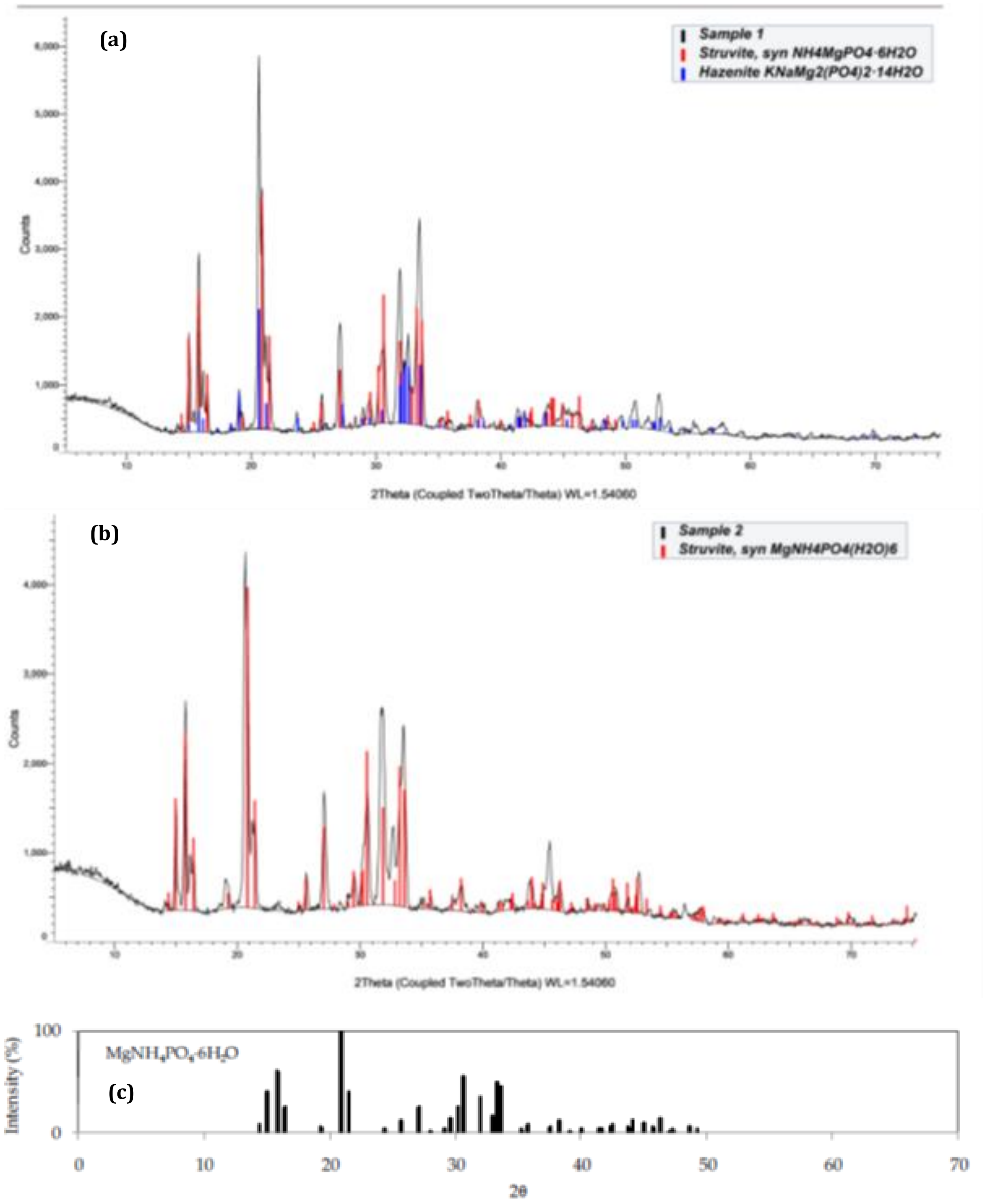


Figure 4. XRD analyses of **(a)** dry struvite precipitate in the molar ratio of N:Mg:P of 1:1:1, **(b)** dry struvite precipitate in the molar ratio of N:Mg:P of 1:1.5:1, and **(c)** pure struvite

4. Result and Discussion

Optimum solubilization of nutrients and metals was obtained at an NaOH concentration above the center point and a temperature below the center point when the L/S ratio was at the center point. NaOH helped denature proteins and ionize inorganic phosphate, which dissolved easily in the aqueous phase. As a result of all applied hydrolysis tests (except 1) in this study, the pH values of the hydrolyzed liquid were >10, which had a higher effect than temperature of increasing NaOH concentrations on PO_4^{3-} and NH_4^+ solubilization from sewage sludge. With an increase in temperature, the solubilization of metals also increased. A temperature below the center point was found to be suitable for metal releases. EDS analyses of hydrolyzed sludge obtained under optimum conditions showed that the mass percentage of C, P, Fe, Al, and K decreased compared to that of the digested sludge.

The concentration of Mg in the hydrolyzed liquid is not enough to make an equal molar ratio with NH_4^+ and PO_4^{3-}. Under optimum conditions, the removal efficiencies of NH_4^+ and PO_4^{3-} from hydrolyzed liquid by precipitation of struvite were 57.43 and 79.22% in the N:Mg:P molar ratio of 1:1:1, and 73.31 and 99.02% in the N:Mg:P molar ratio of 1:1.5:1 at pH 9, respectively. The dry precipitate showed hazenite and struvite formation in the molar ratio of N:Mg:P of 1:1:1. Hazenite is a new struvite compound with a structure containing two separate monovalent K and Na cations. The positive effect of NaOH on K solubilization caused the formation of hazenite. To the best of our knowledge, hazenite was formed for the first time in nutrient recovery from sewage sludge in the present study.

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Conflict of Interest

No conflict of interest was declared by the authors.

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