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CASE STUDY

Phosphorus recovery from domestic sewage sludge in the presence of waste grape pruning biochar

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ABSTRACT

BACKGROUND AND OBJECTIVES: Phosphorus is an essential and limiting nutrient for all living organisms. Although phosphorus is a finite resource on earth, it is usually wasted today. Precipitation of struvite from waste residues is mainly carried out to recover phosphorus. This study aimed to investigate the percentage of phosphorous recovery from sewage sludge in the presence of grape-biochar via the formation of biochar/struvite precipitates.
METHODS: Different amounts of grape-biochar were applied to recover nutrients (phosphorus, nitrogen, and magnesium) from sewage sludge via the formation of struvite by digestion of sewage sludge with H_2SO_4 and the molar ratio of magnesium/ ammonium/ phosphorus in 2:1:1 at pH=8.5. Solubility and release properties of the precipitates were determined and the equations, such as first-order, parabolic diffusion, power function, and simple Elovich models, were fitted to the kinetic data.
FINDINGS: The phosphorus recovery from sewage sludge increased by application of grape biochar in the precipitation system, and the accumulation release of nutrients (phosphorus, nitrogen, and magnesium) from samples increased in the presence of grape biochar, especially in high amounts. Increasing the remove and recovery of phosphorus from sewage sludge by application of grape-biochar decreased the incidence of eutrophication, as an environmental dilemma, and provided the requirement for phosphorus-fertilizers by solid waste management. The solubility of the samples was 0.5 mole per liter hydrochloric acid > in 20 gram per liter citric acid > water. The results showed that the phosphorus- cumulative - release of composites in water good fitted the parabolic kinetic model (R^2=0.97-0.99), whereas it followed the simple Elovich model (R^2=0.86-0.92) in 0.5 mole per liter hydrochloric acid and first-order kinetics model (R^2=0.76-0.92) in 20 gram per liter critic acid.
CONCLUSION: The results indicated that the presence of grape-biochar for recovery of phosphorus from sludge as struvite had a good potential for increasing the release of nutrients for the formation of struvite, and these precipitates had a high potential to be used as a slow-release phosphorus-fertilizer.

NUMBER OF REFERENCES	NUMBER OF FIGURES	NUMBER OF TABLES
47	3	8

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INTRODUCTION

Phosphorus (P) is a key element for life on the earth, facing various limitations for crop production. Being a nonrenewable P source and having different interactions with soil components have attracted the globe's attention to the management of unsustainable P fertilizer (Tosun, 2021). The world's mining of nonrenewable phosphate rock for production of P-fertilizers, such as ammonium phosphates and superphosphates, is running out (Li *et al*., 2018). Therefore, dependency on minable P-sources should be developed procedures for recovering any P-rich resources, especially from residues and secondary raw P (Yetilmezsoy *et al*., 2017). The European Union (EU) confirmed this by putting phosphate rock on its list of critical raw materials in 2014 (Muys *et al*., 2021). Sewage sludge (SS) from municipal solid waste is determined by high value of P_2O_5 (about 4-26%), and nearly 80-90% of P-sewage accumulated in SS (Semerci *et al*., 2020) is determined as a potential p-resource (Adam *et al*., 2009). Accordingly, recovery of the nutrients, especially P and N, from SS has been a noteworthy option and recently received great attention. Chemical precipitation is considered as an important process for recovering the elements (P, Mg, and N) as struvite (magnesium ammonium phosphate hexahydrate), $MgNH_4PO_4.6H_2O$ for reuse of essential ions in SS (Koga 2019; Kim *et al*., 2018). This procedure not only recovers phosphorus, decreasing the emphasis on restricted non-production phosphate rock sources, but also decreases the P content that would, in other ways, be poured into aquatic environments (Rahman *et al*., 2014). P-rich wastewater provides eutrophication and harmful algal blooms which threaten the aquatic ecosystems (Siciliano *et al*., 2016; De *et al*., 2016). Struvite is a P-mineral that can be applied as a slow-releasing agricultural fertilizer by providing Mg, P, and N for plant growth (Muys *et al*., 2021). There are possible benefits in low solubility of struvite in water compared to more soluble conventional P-fertilizers. However, struvite is a root-activated mineral because it has good solubility in acid citric that exudates from roots (Hertzberger *et al*., 2020). Slow-release properties of struvite could reduce losses of nutrients by precipitation and leaching, leading to enhanced crop response to the application of fertilizer (Hertzberger *et al*., 2020). The nutrient release from fertilizers has been specified as a worldwide challenge for the agricultural part in plant nutrition management. The formation of struvite creates in the alkaline range of pH (7<pH<11) and includes 13% P, 6% N, and 10% Mg (Egle *et al*., 2016). The recovery of P content, as struvite, can be influenced by various operating parameters, including pH, the molar ratio of Mg^{2+}: NH_4^+: PO_4^{3-}, time, reaction temperature, organic matter, the presence of other ions, the ratio of liquid/solid (L/S), *etc.* (Doyle and Parsons, 2002). Previous researches on P recovery from P-rich effluent/wastewater and SS have been presented in Table 1. Biochar is determined as an efficient substance for the recovery of surplus nutrients, containing P, from aqueous solutions (Dugdug *et al*., 2018). Biochar is a type of organic material created by the pyrolysis of agricultural wastes and other biomass at 300–1500 °C in oxygen-free conditions, and it has been reported for usage as a P sorbent (Lehmann and Joseph, 2015). Sorption of P by biochar from aqueous solutions accrues through precipitation of P with Mg (Shepherd *et al*., 2016). Increasing sorption of P by application of biochar can be due to its high surface area and AEC (anion exchange capacity) (Lehmann *et al*., 2015). Many materials were recommended for increasing the recycling efficiency for the formation of struvite, including quartz, steel mesh, pumice, and borosilicate glass (Le Corre *et al*., 2007). Consumption of the biochar with high surface area, CEC (cation exchange capacity) and porosity is eco-friendly in the crystallization of struvite to ameliorate nutrient recovery for application of fertilizer and can be used as a good strategy (Muhmood *et al*., 2019). Hu *et al*., (2019) reported the recovery rates of P, Mg, and N increased for precipitation of struvite by application of the biochar obtained from straw and wheat shells. Muhmood *et al*., (2019) showed that wheat straw biochar and rice husk biochar as seeding materials in the precipitation of the struvite from digested chicken slurry increased the formation of struvite and intensified element recovery. Enhancing the recovery of nutrients is necessary to examine many eco-friendly materials, such as biochar of grape residues (Gr) from pruning manufactured in high amounts in vineyards, in struvite precipitation process. To the best of the authors' knowledge, the use of Gr-biochar, as seeding material, in the struvite

Table 1: Summary of the recent studies about P-recovery

Relevant aspects	References
The current study was designed to use a different light spectrum to enhance carbon-based metal nanocomposites adsorbent for the augmented removal of nitrate and phosphate from aqueous solution. The revealed nanocomposites increased the removal of nitrate and phosphate ions up to 95%.	Velu *et al.,* (2020)
Acceptable phosphorus recovery (80-90%) was achievable by using seawater as the magnesium source for struvite precipitation. The increase of temperature from 20 °C to 30 °C reduced the phosphorus recovery.	Shaddel *et al.,* (2020)
This manuscript provides a comprehensive review on the recent developments related to the removal and recovery of nutrients (nitrogen and phosphorus) from aqueous waste and wastewater.	Siciliano *et al.,* (2020)
This paper reviews the recent studies on the potential of aquatic plants, such as free-floating, submerged, and emergent plants, and microalgae for the removal of P in different types of wastewater.	Rezania *et al.,* (2021)
The P extraction from P-rich sludge with oxalic acid proved to be effective for P- extraction and iron removal prior to struvite precipitation. Due to the high iron concentration in liquor, the product of direct precipitation contains a high amount of iron that limits its use as phosphate fertilizer.	Numviyimana *et al.*, (2022)

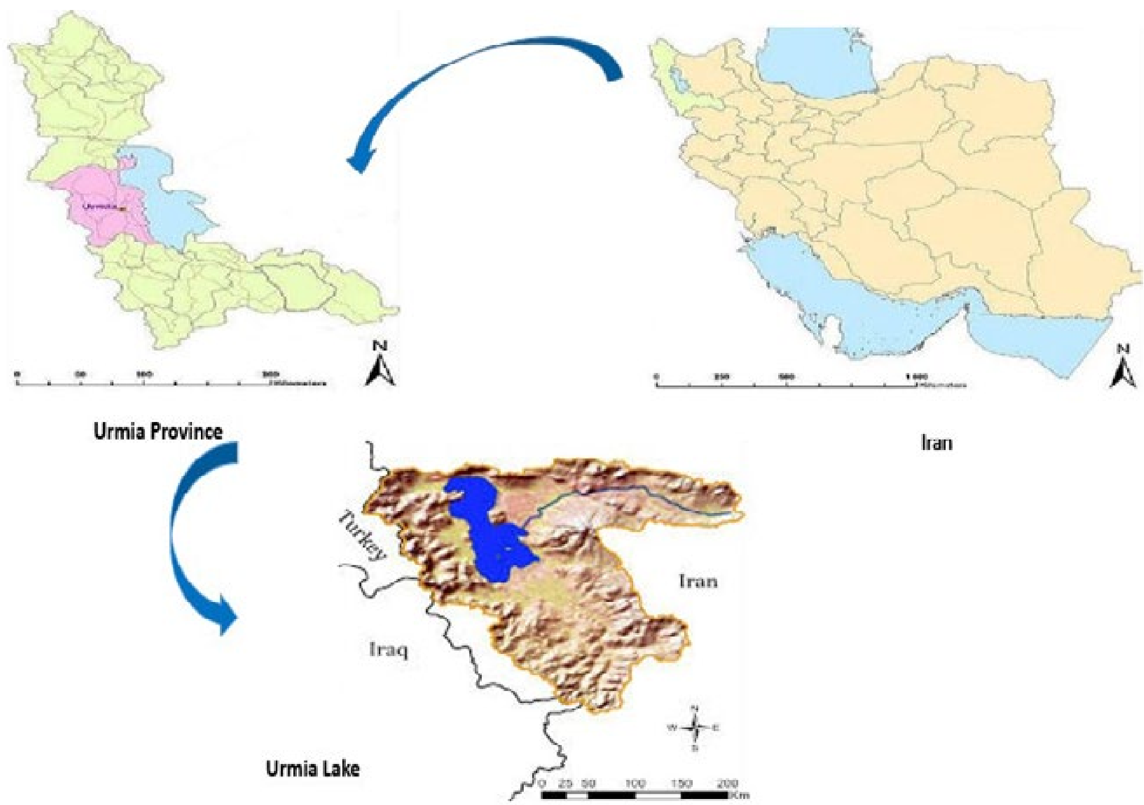


Fig. 1: Geographic location of the study area in Urmia, West Azerbaijan province, Iran

precipitation process has not been investigated yet. The objectives of this study were to: 1) reuse P as struvite and composites of struvite/biochar from sewage sludge; 2) investigate the efficacy of different values of Gr-biochar on the recovery of nutrients (P, N, and Mg); and 3) study the ability of P, Mg, and N ions to be dissolved and examine their slow-release-properties in composites of struvite/ biochar. This study aimed to contribute to the environmentally friendly process of P-recovery via struvite precipitation by solid waste management. This study was carried out at the Soil Department of Urmia University, Urmia, Iran, during 2021-2022.

MATERIALS AND METHODS

Preparation of sewage sludge (SS) and biochar of grape residues (Gr-biochar)

Dewatered sewage sludge (SS) was sampled from a domestic wastewater treatment plant in Urmia (37° 35’ 37.1” N 45° 07’ 43.7” E), West Azerbaijan Province, Iran (Fig. 1).

The SS was air-dried and sieved to pass a 1 mm. Some physicochemical properties of SS, such as total organic carbon (TOC), electrical conductivity (EC), pH, total nitrogen (TN), ammonia nitrogen (NH_4^+-N), total phosphorus (TP), orthophosphate (PO_4^{3-}-P) and potassium content (K), were determined according to Semerci *et al.,* (2019). Total recoverable concentrations of metals (Ca, Mg, Na, Fe, Zn, Cu, Pb, and Cd) were also determined (Malwina, 2019). The grape pruning residues applied to prepare biochar were collected from vineyards in the West Azerbaijan Province, Iran. The grape cane was cut into small pieces and put into an oxygen-free cast iron bioreactor. The Gr-biochar was gathered by pyrolysis at 500 degrees Celsius (°C) at 10 degrees Celsius per minute (°C/min) heating rate for 2 hours (h). The prepared Gr-biochar was then ground and sieved (through a 0.5 mm sieve) for application as seeding materials for the production of struvite. The Gr-biochar was analyzed for some physicochemical properties.

P-extraction experiment

To extract P from SS, two steps were carried out: 1) digestion of H_2SO_4 0.2 N (98% Merck, Germany) into a solid to liquid ratio of 1:10; 2) precipitation. Prior to P-precipitation, citric acid ($C_6H_8O_7$) (50% w/v) (Sigma-Aldrich) was added, as a chelating agent, for the removal of heavy metals. Using sodium hydroxide (NaOH) 5N (>98% Sigma-Aldrich), the potential of hydrogen (pH) of the solution raised to 8.5 after adding $MgCl_2.6H_2O$ (Sigma-Aldrich) as Mg source (Meyer *et al.*, 2015). The precipitation was conducted at 2:1:1 molar ratios of Mg^{2+} /PO_4^{3-}/ NH^{4+} respectively, at room temperature and stirring speed of 150 rpm for 30 min, and finally stayed for 30 min for reacting. Then, the solution rested for 30 min to influence the precipitation of struvite (Huang *et al*., 2015). Samples were filtered through Whatman No. 42 and allowed oven-dried at 40 °C for 48 h, weighed, and applied for analyzing the nutrient and metal contents. To obtain struvite/ biochar precipitations, the Gr-biochar was used in 0, 2.33, 7, and 21 g of Gr-biochar (the ratios of the struvite mass to GR-biochar of 0%:100%, 75%:25%, 50%:50%, and 25%:75%). After shaking the solution for 30 min and leaving to rest for 24 h at room temperature (Hu *et al*., 2019), it was washed up to pH of 7. The P-recovery was evaluated using Eq. 1.

$$\text{P-recovery\%} = \left(\frac{P_i - P_F}{P_i}\right)\times 100 \quad (1)$$

Where, P_i is the initial concentration of P mg/L; and P_F is the final concentration of P mg/L.

The composites of struvite/biochar were analyzed by XRF for the determination of chemical composition. Content of the metals was determined by inductively coupled plasma optical emission spectroscopy (Varian, Vista-Pro-ICP-OES). Surface morphology of precipitates was recognized by Scanning Electron Microscopy (SEM- XL 30-Philips).

Solubility struvite/ GR-biochar composites

The HG 2598-94 protocol was applied to determine the solubility of the precipitates (Hu *et al*., 2019). One gram of the precipitates, 150 mL of HCl 0.50 mole per liter (mol/L) (98% Sigma-Aldrich) and 20 gram per liter (g/L) of citric acid (CA) were applied, respectively. Then, the solution was shaken in a 250-mL volumetric flask (80 min at 180 rpm), and the P contents in the samples were evaluated by an ultraviolet light (UV) spectrophotometer (Shimadzu UV3100) by monitoring the absorbance changes at 470 nanometers (nm). The Mg content was assessed by the titrimetric method using Ethylene diamine tetra acetic acid (EDTA) (99%- Sigma-Aldrich). To determine the N-concentration, the titrimetric method was applied after distillation.

Kinetics and slow-release properties

Release properties of the samples were evaluated according to the GB 23348 2009 protocol (Hu *et al*. 2018). One gram of each precipitate was added to 20 mL of deionized water in a 50-mL volumetric flask and placed in an incubator at 25 °C. To determine the amounts of N, P, and Mg in the solutions, they were filtered in intervals of 24 h after 3, 5, 10, 14, 28, 42, 56, and 84 days. The cumulative release values (%) of N, P and Mg were determined according to Eq. 2.

$$\text{Accumulative release (\%)} = \frac{C_t \times V}{M_{total}} \times 100 \qquad (2)$$

Where, c_t is the concentration of N, Mg and P (mg/kg) at different times; and M_{total} is the total nutrient amount in the sample. To evaluate the release mechanism of the elements, four kinetic equations, including the first order (Eq. 3), power function (Eq. 4), parabolic diffusion (Eq. 5), and simple Elovich models (Eq. 6), were applied to fit the results (Jalali 2006).

$$\text{First–order model: } \ln(q_0 - q_t) = a - bt \qquad (3)$$

$$\text{Power function model: } lnq = lna + b\,lnt \qquad (4)$$

$$\text{Parabolic diffusion model: } q = a + bt^{1/2} \qquad (5)$$

$$\text{Elovich model: } q = a + lnt \qquad (6)$$

Where, *q* is the cumulative release of the elements; *t* is the time of release; and *a* and *b* are the constants of the equations. *b* is an essential parameter in these models, which shows the release rate of the ions. The coefficients of determination (R^2) were applied to determine the best model describing the release mechanism process.

RESULTS AND DISCUSSION

Properties of SS and Gr-biochar

Some characteristics of the SS are presented in Tables 2 and 3. The total phosphorus and total nitrogen in SS were more than 1.5%. The main chemical composites of SS were SiO_2, CaO, P_2O_5, Fe_2O_3, and Al_2O_3 (Table 3). The P_2O_5 content in the SS sample had a potential of P-source and providing source conservation (Shiba and Ntuli, 2016; Adam *et al*., 2009). The pH and EC of SS were 6.6 and 1.79, respectively.

The amount of heavy metals (Pb, Cd, Zn, Cr, Cu and Ni) in SS was lower than the standard concentration limit in sludge as using fertilizer (Xu *et al*., 2012). The total ratio of aluminum and iron to phosphorus is a valuable index for the P-supplying power of a SS (Shiba and Ntuli, 2016). The molar ratio of the sum of the aluminum and iron to phosphorus is an okay indicator for the P-reserving power of a SS, with amounts < 1 being characteristic of a SS able to supply high amounts of soluble P (Pastene, 1981). The molar ratio of Al + Fe/P for the SS applied in this study was obtained to be more than the ratio reported based on ICP results (Table 2), indicating a meager potential for P-supply. This factor determined the limitation for direct application of the SS as a fertilizer.

The physicochemical properties of GR-biochar and other biochars are presented in Table 4. Surface area of the Gr-biochar was 277 m^2/g, and its pH was 9.6, suggesting an alkaline characteristic. Evidently, the pH of the Gr-biochar was different from the pH of the wheat shell and other biochars (Hu *et al*., 2019; Lu *et al*. 2016; Park *et al*., 2011).

Table 2: Chemical properties of sewage sludge

pH	$EC_{(1:5)}$	TOC (%)		TP	NH_4^+-N	TN	Mg	Na	K	Moisture
	dS/m				mg/kg					%
6.6	1.79	48		15927	904	18605	6513	2967	11207	14.03
					Total concentration of metals (mg/kg)					
Pb	Cd		Fe	Zn	Al	Cr	As	Cu	Ni	Ag
57	0.32		13230	731	21063	18	1.9	179	30	2.3
					Heavy metal concentration limit (EPA 503)					
750-1200	20-40		-	2500-4000	-	25	-	1000-1750	300-400	-

EC: electrical conductivity; PO_4^{3-}–P: orthophosphate; TP: total phosphorus; TN: total nitrogen; TOC: total organic carbon

Table 3: Chemical composition of sewage sludge

Constituent	Sample	Adam *et al.* (2009)	Ntuli *et al.* (2013)	Shiba and Ntuli (2016)
P_2O_5	4.00	3-25	14.6	15.2
SiO_2	14.48	13-43	38.4	36.40
CaO	11.33	12-18	11.0	11.3
Fe_2O_3	1.89	3.2-22	10.3	12.2
SO_3	1.57	-	5.5	5.31
Al_2O_3	3.93	8-24	11.9	12.0
MgO	1.08	1.7-3.5	1.7	1.04
K_2O	1.35	0.95-2.7	1.7	1.79
MnO	<0.05	0.09-0.35	0.6	0.613
TiO_2	0.32	-	1.1	1.16

Table 4: Some properties of Gr-biochar

Biochar	pH	EC (dS/m)	C	N	H	CEC ($cmol_c$/kg)	Surface aria (m^2/g)	Ash (%)	References
Grape	9.6	0.2	71	0.87	2.9	34	277	11	This study
wheat shell	7.3	-	-	-	-	77.8	168.3	-	Hu *et al.*, 2019
Rice straw	10.1	-	51	1.66	1.70	43	37	-	Lu *et al.*, 2016
Green waste	7.7	-	77	0.26	2.6	250	6.87		Park *et al.*, 2011

EC: electrical conductivity; CEC: cation exchange capacity.

Table 5: Chemical analysis of composites (struvite:Gr-biochar)

Struvite (%): Biochar (%)	SiO_2	Al_2O_3	BaO	P_2O_5	Fe_2O_3	MgO	Na_2O	SO_3	K_2O	CaO	TiO_2
					(%)						
100:0	0.53	1.05	<0.05	28.19	2.77	16.51	1.45	1.38	1.59	14.77	<0.05
75:25	1.36	0.86	<0.05	25.40	0.30	11.53	0.85	2.36	0.22	14.27	<0.05
50:50	0.72	0.75	<0.05	22.63	0.16	10.23	1.06	0.78	0.34	9.32	<0.05
25:75	0.43	0.65	<0.05	13.44	0.43	7.17	1.37	1.30	0.65	4.22	<0.05

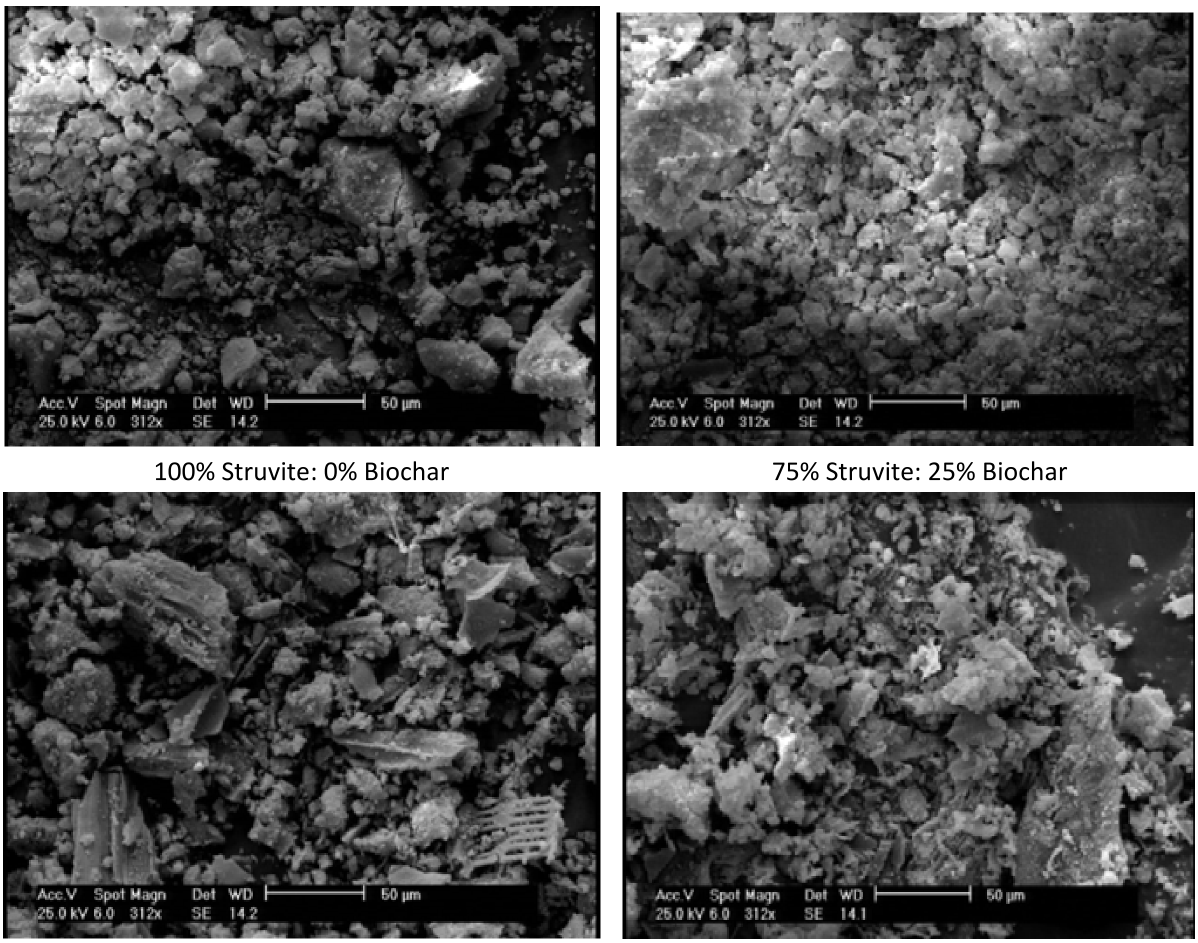
Table 6: Properties of composites (struvite: biochar)

Parameter	%struvite:%biochar				EU fertilizer limit (Muys *et al.*, 2021)
%	100:0	75:25	50:50	25:75	
P	12.67	10.36	9.38	6.27	-
N	8.40	7.46	5.60	4.60	-
Mg	9.88	7.87	6.14	4.89	-
K	1.20	0.26	0.40	0.78	-
SI	4.74	6.25	9.63	11.24	-
$pH_{(1:10)}$	7.48	8.23	8.32	8.43	-
$EC_{(1:10)}$ (dS/m)	3.15	4.15	6.39	7.46	-
Cd (mg/kg)	2.80	1.80	1.90	2.40	60
Pb (mg/kg)	7	6	16	19	120
Cu (mg/kg)	16	37	43	51	600
Zn (mg/kg)	900	1011	1132	1321	1500
AS (mg/kg)	29.30	32.10	33.90	37.14	40
Mo (mg/kg)	0.55	0.57	0.87	1.19	-
Ni (mg/kg)	13	13	14	15	

SI: salt index, EC= electrical conductivity

Table 7: Solubility of samples in water, citric acid, and HCl

Struvite (%): Biochar (%)	Solution	P (g/L)	Dissolution rate (%)	N (g/L)	Dissolution rate (%)	Mg (g/L)	Dissolution rate (%)
	water	1.35	1.06	0.046	5.50	0.0096	1.45
100:0	20 g/L citric acid	77.88	61.43	0.17	20.41	0.4464	67.71
	0.5 mol/L HCl	104.05	82.08	0.23	27.32	0.648	98.30
	water	1.16	1.12	0.047	6.31	0.0096	1.82
75:25	20 g/L citric acid	73.51	70.89	0.18	33.34	0.3793	72.20
	0.5 mol/L HCl	90.95	87.71	0.25	33.24	0.520	99.69
	water	1.09	1.16	0.048	8.56	0.0096	2.34
50:50	20 g/L citric acid	78.24	83.41	0.19	33.62	0.2976	72.20
	0.5 mol/L HCl	85.16	90.79	0.26	45.78	0.40	99.60
	water	0.83	1.33	0.50	10.78	0.0096	2.94
25:75	20 g/L citric acid	54.94	87.55	0.19	45.32	0.2544	77.90
	0.5 mol/L HCl	57.12	91.03	0.28	59.90	0.32	100



100% Struvite: 0% Biochar

75% Struvite: 25% Biochar

50% Struvite: 50% Biochar

25% Struvite: 75% Biochar

Fig. 2: Scanning Electron Microscopy of samples

Fig. 3:

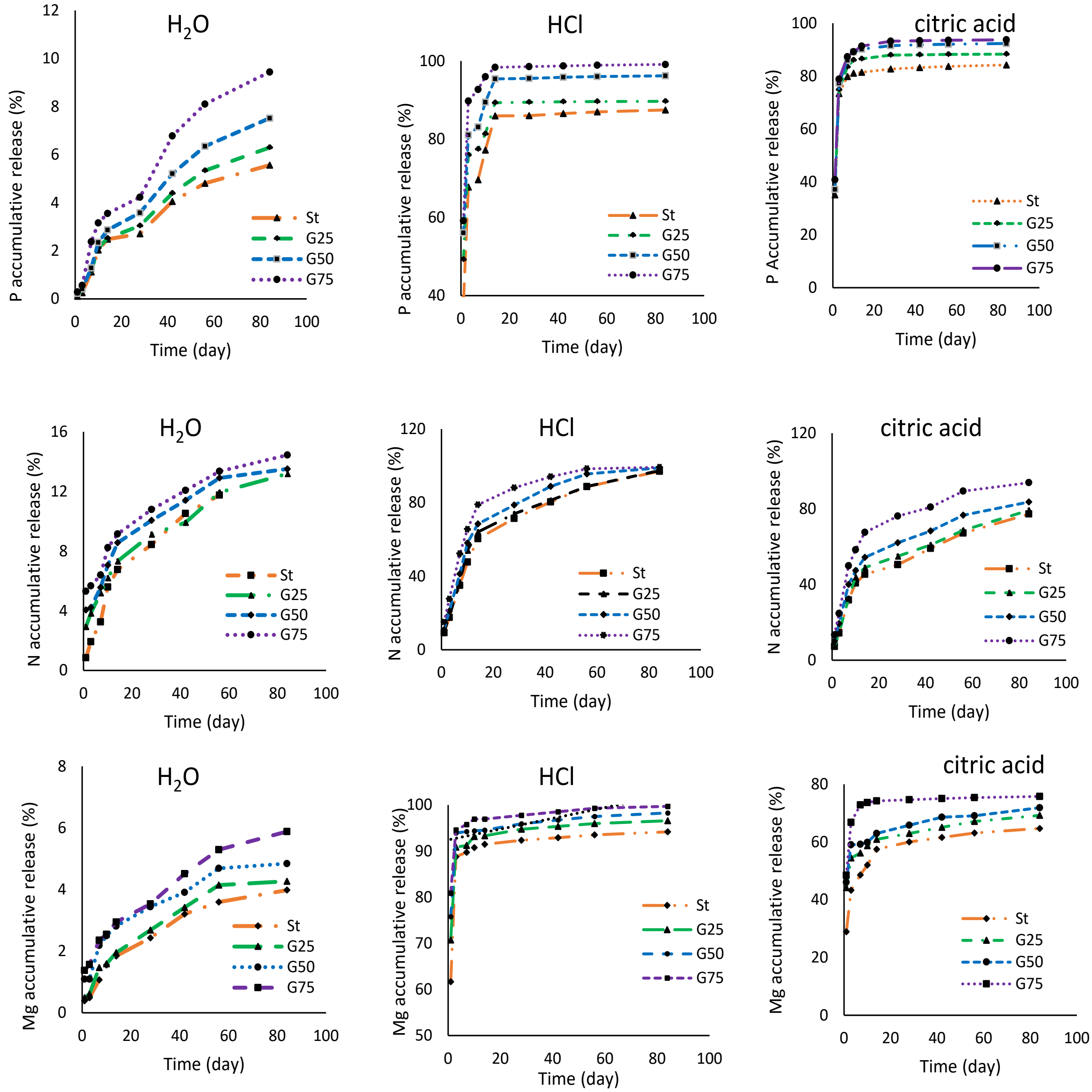


Fig. 3: Cumulative releases of P, N, and Mg from differente %Struvite:%Bbiochar (100:0 (St), 75:25 (G25), 50:50 (G50), 25:75 (G75)) in water, 20 g/L citric acid and 0.5 mol/L HCl.

P- Precipitates

The XRF results of the samples are presented in Table 5. Amount of P_2O_5 for %struvite: %Gr-biochar of 100:25, 75:25, 50:50 and 25:75 were 28, 25, 22, and 13%, respectively. This could be due to the presence of other particles such as Fe, Al and biochars (Rahman *et al.*, 2014; Shiba and Freeman, 2016). The amount of MgO in the samples decreased by increasing the amount of Gr-biochar. Shiba and Ntuli (2016) reported that the amount of P_2O_5 in the struvite from sewage sludge in different conditions was from 14.0 to 32.50%. Also, Hu *et al.*, (2019) showed that the amount of P_2O_5 in the samples was in the range of 22 and 30%. P-amount generally ranges as 11–26% in struvite by deferent precipitation methods (Johnston and Richards, 2003; Khan *et al.*, 2019).

Table 8: Parameters of kinetic models for P release from the samples in water, HCL and citric acid

Equation	Water			0.5 mol/L HCL			20 g/L citric acid		
First-order	R^2	a	b	R^2	a	b	R^2	a	b
St	0.95	1.66	0.031	0.82	2.62	0.06	0.92	1.84	0.05
G25	0.95	1.79	0.029	0.83	2.24	0.10	0.92	1.87	0.08
G50	0.96	1.99	0.029	0.84	2.30	0.07	0.92	2.063	0.06
G75	0.94	2.19	0.030	0.84	1.69	0.06	0.76	2.18	0.0
	Water			0.5 mol/L HCL			20 g/L citric acid		
Power function	R^2	a	b	R^2	a	b	R^2	a	b
St	0.94	0.94	0.63	0.89	4.33	0.05	0.87	11.46	0.02
G25	0.97	6.23	0.58	0.86	11.35	0.04	0.81	11.30	0.03
G50	0.97	6.18	0.62	0.89	11.27	0.04	0.85	11.23	0.04
G75	0.92	6.21	0.56	0.91	10.95	0.02	0.88	10.84	0.04
	Water			0.5 mol/L HCL			20 g/L citric acid		
Parabolic	R^2	a	b	R^2	a	b	R^2	a	b
St	0.98	-0.122	0.63	0.74	78.35	2.49	0.70	76.35	1.01
G25	0.98	-0.22	0.71	0.72	83.67	1.78	0.58	79.70	1.21
G50	0.99	-0.41	0.86	0.72	85.22	1.86	0.63	82.03	1.42
G75	0.97	-0.21	1.040	0.71	91.61	1.03	0.67	83.08	1.46
	Water			0.5 mol/L HCL			20 g/L citric acid		
Elovich	R^2	a	b	R^2	a	b	R^2	a	b
St	0.92	-0.20	1.14	0.89	76.41	3.12	0.88	75.40	2.14
G25	0.89	-0.26	1.27	0.86	82.29	3.65	0.82	78.17	2.70
G50	0.88	-0.44	1.53	0.89	83.60	3.89	0.87	80.39	3.11
G75	0.86	-0.23	1.85	0.92	90.60	4.19	0.88	81.55	3.15

The NPK fertilizers must have 5 to 12% of P_2O_5, and the PK fertilizers must have 18 to 20% P_2O_5 (Adam, 2009). Precipitates in this study were appropriate for creating P fertilizers from secondary raw materials and could be applied to preserve rock phosphates and contribute to source protection. However, %struvite: %biochar samples contained both valuable elements (P, Mg, N and K) and carriers of heavy metals (Table 6).

Generally, struvite ($MgNH_4PO_4.6H_2O$) has 6% N, 13% P, and 10% Mg (Rahman *et al*., 2013). The concentration of heavy metals in struvite/biochar samples was lower than the permissible limit (Table 6). As already described, the content of metals increased by increasing the amount of Gr-biochar in the samples probably due to either sorption or co-precipitation (Muhmood *et al*., 2019; Ma and Rouff, 2012; Uysal *et al*., 2014). In addition, biochar has been used to immobilize heavy metals (Lu *et al*., 2017; Wu *et al*., 2017; O'Connor *et al*., 2018) and increase nutrient availability (Li *et al*., 2019). The SEM of precipitates exhibited that the particles had a rod-like shape (Fig. 2) and this was consistent with the results detected by Rahman *et al*., (2014), Shiba and Freeman (2016), and Hu *et al*., (2019). P-recovery at pH=8.5 and in %struvite: %biochar ratios of 100:25, 75:25, 50:50 and 25:75 were 92, 92, 93 and 96%, respectively. Similarly, Kobar *et al*., (2020) reported that recovery of P and N from biogas slurry increased by 71 and 94%, respectively, with the incorporation of rice-biochar and struvite. Zheng *et al*., (2018) found that N and P recoveries from urine intensified by nearly 40–50% and 97% by combining biochar and struvite at pH=9, respectively. High surface area and high CEC of biochar may be valuable for adsorbing N and P from wastewater and reducing their losses (Kobar *et al*., 2020).

Solubility and kinetic properties of samples

The solubility of the samples in deferent amounts of the Gr-biochar was calculated by the procedure determined previously. The solubility results of the samples in water, CA, and HCl are shown in Table 7. The solubility was higher in HCl and CA than in water. The amount of P, Mg and N in the samples were in an order of 100% struvite > 75% struvite: 25% Gr-biochar > 50% struvite: 50% Gr-biochar > 25% struvite=75% Gr-biochar (Table 7). Thus, the extracted concentrations of P, Mg and N were the same, but their dissolution rate increased by increasing the Gr-biochar, indicating that the Gr-biochar could intensify the release properties of P-precipitates. Dong *et al*., (2020) reported that the biochar-based slow-release fertilizer, which included natural materials, not only reduced N-leaching, but also supplied a high amount of N to the rice plant in later stages of the production cycle.

The accumulative P, Mg and N releases from precipitates began with a rapid reaction and followed by a slow reaction (Fig. 3). The accumulative release nutrients from samples were as follows: 25% struvite=75% Gr-biochar (G75) > 50% struvite: 50% Gr-biochar (G50) > 75% struvite: 25% Gr-biochar (G25) > 100% struvite (St) (Fig. 3). The initial fast release of ions was a characteristic of their high lability, whereas the slow fraction could be related to their low mobility (Hosseinpur, 2011). The initial rapid reaction was related to the rapid release of poorly crystalline phosphates in the precipitates, especially with a high amount of Gr-biochar, which were metastable ions and rapidly released. Gr-biochar, with a high surface area, had a high efficacy on the adsorption of ions during precipitation of samples. The P-accumulative releases in water from St, G25, G50, and G75 were 5.57, 6.30, 7.52, and 9.44%, respectively, and P-releases of them in 20 g/L CA were 84, 88, 92, and 94% respectively, and in 0.5 mol/L HCl were 87, 90, 96, and 99%, respectively, after 84 days. The Mg and N-accumulative releases from the mentioned samples followed the same trend. The accumulative release of nutrients was higher in 0.5 mol/L HCl (pH=0.3) than in water and CA (20 g/L) (pH~3). Since, struvite is a root-activated fertilizer, increasing the release of phosphorus from its compounds in the presence of Gr-biochar, especially in CA solution, can be effective in the early stages of plant growth to provide P, which requires greenhouse studies.

The P-release results from samples in water, CA (20 g/L), and HCl (0.5 mol/L) solutions were fitted to the first-order, power function, parabolic diffusion, and simple Elovich models presented in Table 8. The parabolic model with a high R^2 (R^2= 0.97-0.98) represents the P-cumulative release from samples in water (Table 8). The parabolic kinetic model indicated that the release of P from these precipitates in water was controlled by the diffusion process (Hosseinpur, 2011). Also, the P-releases in the samples well fitted to the Elovich model in HCl solution and the first-order model in CA solution well described them. This was consistent with results reported by other researchers (Hu *et al*., 2019; Jalali, 2006). The b parameter showed the slope and it could be applied as an index for the release of P from the samples. Based on the Elovich equation, the release rates of P from the samples were as follows: HCl> CA> water. The parameters of this model increased by increasing the amount of the Gr-biochar (G75> G50> G25> St), implying that high amount of Gr-biochar could intensify P-release from precipitates. Wang *et al*., (2010) reported that the Elovich equation could explain a lot of reaction mechanisms including not only the diffusion of P-released at the surface or interface, but also the activation energy and deactivation of the surface. Kong *et al*., (2020) reported that the first-order, and the Elovich models could well fit the kinetic data in P-release from a fish feed.

CONCLUSION

In this study, the values of heavy metals in sewage sludge were lower than the standard limits in sludge using fertilizer, while the molar ratio of Al + Fe/P of SS was more than the standard limits indicating its low potential to be directly used as P-fertilizer. Increasing Gr-biochar for the removal of P from SS increased the P-recovery. Moreover, the value of heavy metals in precipitates increased in the presence of Gr-biochar, but their values were lower than the permissible limit. The nutrient's accumulative releases from the samples were as follows: G75 > G50> G25 > St. The accumulative release of P, Mg and N from the samples began with a rapid reaction and followed by a slow reaction. The highest solubility of the samples was observed in HCl and then in CA, and water. The parabolic model good described the P-cumulative release from composites in water. It followed the Elovich model in 0.5 mol/L HCl solutions and the first-order equation in 20 g/L CA. The amount of P_2O_5 in the precipitates was higher than 12%, indicating that these precipitates could be applied as P-fertilizer. This study showed the efficiency of P-recovery from SS in the presence of the Gr-biochar by struvite precipitation and then provided a sustainable matter for agriculture. The precipitation method applied in this study could help in solving the difficulties of disposing SS. Before planning for

P-recovery by biochar/struvite composites, further different options of P- recovery should be analyzed for their cost and environmental efficiency. The accumulation of heavy metals in Gr-biochar/struvite precipitates from SS should be further explored in greater detail in future research for P-recovery from wastewater with a high amount of heavy metal. Furthermore, field experimentation would be needed to determine the effectiveness of these P-precipitates fertilizers for many types of soils and cropping systems in future studies.

AUTHOR CONTRIBUTIONS

M. Piri performed the literature review, analyzed and interpreted the data, prepared the manuscript text, and manuscript edition. E. Sepehr performed the literature review, data analysis and manuscript preparation as well as provided critical revision of the manuscript.

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CONFLICT OF INTEREST

The authors declare no potential conflict of interest regarding the publication of this work. In addition, the ethical issues including plagiarism, informed consent, misconduct, data fabrication and, or falsification, double publication and, or submission, and redundancy have been completely witnessed by the authors

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ABBREVIATIONS

Ag	Silver
As	Arsenic
Al_2O_3	Aluminum oxide
Ca	Calcium
Cu	Copper
Cr	chromium
C	Carbon
CEC	Cation exchange capacity
Cd	Cadmium
ºC	Degree Celsius
CaO	Calcium oxide
Cº/min	degree Celsius per minute
Eq.	Equation
EC	electrical conductivity
EDTA	Ethylene diamine tetra acetic acid
CA	citric acid
Fe	Iron
Fig.	Figure
Fe_2O_3	Iron (III) oxide
g/L	gram per liter
Gr-biochar	biochar of grape residues
HCl	Hydrochloric acid
H	Hydrogen
h	Hour
H_2SO_4	Sulfuric acid
K_2O	Potassium oxide
K	Potassium
mg/L	milligrams per liter

Mg	Magnesium
mm	millimeter
mg/kg	milligram per kilogram
mol/L	mole per liter
MnO	Manganese (II) oxide
MgO	Magnesium oxide
nm	nanometer
N	Nitrogen
Na	Sodium
Ni	Nickel
NH_4^+	Ammonium
N	Normality
NaOH	Sodium hydroxide
Pb	Lead
P	Phosphorus
pH	Potential of hydrogen
P_2O_5	Phosphorus pentoxide
R^2	R-squred
SS	*Sewage sludge*
SiO_2	Silicon dioxide
SO_4	sulfate
SI	salt index
TOC	total organic carbon
TN	total nitrogen
TP	total phosphorus
TiO_2	Titanium dioxide
UV	ultraviolet light
Zn	Zinc

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