The study of the ratio of zeolite and humic acid to the properties and nutrient release of hydrogel synthesized from okra mucilage

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Abstract

This study aimed to investigate the effect of different zeolite-to-humic acid ratios on the properties of hydrogel synthesized from okra mucilage for use as a slow-release fertilizer, as well as their influence on nutrient release. The hydrogel was prepared primarily from natural materials by using okra mucilage as the base material and enhancing its performance through the incorporation of zeolite and humic acid at different ratios. The hydrogel was then evaluated for its water-holding capacity, gel fraction, and nutrient release behavior of NPK fertilizer in soil. The results indicated that the addition of zeolite significantly improved the water retention capacity and structural stability of the hydrogel, making it more suitable for controlled nutrient release. Meanwhile, the incorporation of humic acid enhanced nutrient transfer from the soil to plants, thereby improving nutrient uptake and utilization. An appropriate ratio of zeolite to humic acid enabled the hydrogel to effectively regulate nutrient release while prolonging its degradation period. Therefore, the developed hydrogel shows strong potential as a slow-release fertilizer system that can reduce nutrient loss, improve fertilizer use efficiency, and minimize environmental impacts.

keywords: okra mucilage, hydrogel, zeolite, humic acid, slow-release fertilizer

Introduction

Thailand is an agricultural country where chemical fertilizers are widely used to increase crop yield. However, excessive fertilizer use leads to soil degradation and nutrient loss through leaching or conversion into unavailable forms, reducing nutrient uptake by plants. Consequently, farmers must apply more fertilizer, increasing production costs and causing further environmental impacts.

Slow-release fertilizers provide nutrients gradually according to plant demand, reducing nutrient loss, fertilization frequency, and production costs (Thongchai et al., 2011; Amkha et al., 2009).

Hydrogels are three-dimensional polymer materials capable of absorbing and retaining large amounts of water and nutrients, making them suitable for slow-release fertilizer applications. Unlike synthetic hydrogels, okra mucilage is a natural polysaccharide with high viscosity, excellent water absorption, biodegradability, low toxicity, and low cost, making it an environmentally friendly alternative (Chanikarn et al., 2022).

Zeolite improves hydrogel structure, water retention, and nutrient-release control by reducing nutrient loss, while humic acid enhances nutrient availability through chelation and further improves the hydrogel's water-holding properties (Phatthanant et al., 2022).

Therefore, this study aims to determine the optimal ratio of zeolite and humic acid in okra mucilage-based hydrogel to achieve high water retention, controlled nutrient release, and biodegradability for environmentally friendly slow-release fertilizer applications.

Methodology

Part 1: Studying the sedimentation of mucilage using different methods affects the physical and chemical properties of mucilage from okra.

1.1) Extract mucilage from okra.

Cut fresh okra into pieces and dry about 50 grams. Boil with 1.5 liters of distilled water at 60°C for 4 hours. Filter through muslin cloth and let it cool to room temperature.

1.2) Precipitation of mucilage from okra.

Split into two experiments: Precipitate mucilage with 95% ethanol and with 95% acetone at the same volume ratio of 1:1. Filter through muslin cloth and then cool to room temperature. Dry to constant weight at 45°C in a hot air oven., Grind into fine powder with a mortar and pestle. Sieve through an 80 Mesh screen.

1.3) Analysis of the chemical structural components of mucilage using ATR-FTIR.

1.4) Measure the pH of mucilage

1.5) Water holding capacity (WHC) of mucilage.

Dry mucilage weight: 0.5 grams. Add distilled water more than 20 times the weight of the sample Shake with vortex until homogeneous let swell at room temperature for 1 hour, Centrifuge at 3,000 – 4,000 rpm for 20 minutes. Remove excess water Weigh the "water-retained sample" using the formula

$$WHC(g/g) = (W_1 - W_2) / W_1$$

(W_1 = weight of the sample before drying

W_2 = weight of the sample after drying)

Part 2: Study of different ratios on the physical and chemical properties of hydrogels.

2.1) Synthesis of hydrogels from okra mucilage mixed with humic acid and zeolite.

Dissolve 2 g mucilage in 20 mL distilled water. Grind zeolite into fine powder, pass through a 30-mesh sieve. Mix mucilage with zeolite and humic acid at ratios 1:1, 1:2, 2:1. Stir until smooth. Drop citric acid to crosslink while stirring at room temperature. Place on a Petri dish to react.Dry at 40°C for 40-45 hours. Result: hydrogel with different humic acid and zeolite ratios (0:0, 1:1, 1:2, 2:1).

2.2) Test of the gel structure content of hydrogel at different ratios.

Immerse 0.2 g dried hydrogel in 25 mL distilled water at room temperature.Shake at 50 rpm for 24 hours to dissolve uncrosslinked parts. Filter to collect insoluble residue. Dry insoluble part at 100°C and weigh it. Then, calculate the gel fraction using the following formula:

$$\text{Gel fraction } (\%) = (Wd / Wi) \times 100$$

Wd = Dry weight of the water-insoluble part after soaking in distilled water for 24 hours.

Wi = Initial weight of the dried hydrogel before soaking in water.

2.3) Testing of the liquid absorption capacity of hydrogel under free-swelling conditions at different ratios.

Weigh 0.1 g dry hydrogel, put in a tea bag, and immerse in 25 mL test solution at room temperature. Weigh the swollen hydrogel at different times. Calculate absorption capacity using the appropriate formula.

Free absorption capacity = (Ws – Wd) / Wd

Ws = Weight of the swollen hydrogel at time after immersion in the test liquid.

Wd = dry weight of the hydrogel before immersion in distilled water.

Part 3: Fertilizer release test of hydrogel synthesized from mucilage of okra at different ratios.

3.1) Preparation of soil samples for fertilizer release test of hydrogel at different ratios.

Prepare fertilizer solution by dissolving 1 g of NPK in 100 mL water. Mix 2 g of hydrogel in the solution for 1 hours. Dry soil at 82°C for 30 min, weigh, and bury in 50 g soil. Place a 1x1 cm hydrogel piece in a tea bag at 5 cm depth. Arranged as 4, 8, and 12 days.

3.2) Analysis of weight changes of hydrogels with different ratios every 2 days.

3.3) Analysis of P and K nutrient content in soil using ICP-OES instrument.

3.4) Analyze the nitrogen (N) content in soil using CHN Analyzer

Result and Discussion

Part 1: Studying the sedimentation of mucilage using different methods affects the physical and chemical properties of mucilage.

1.1) The results of the chemical structural components of mucilage using ATR-FTIR.

The graph shows the IR absorption spectra of mucilage extracts precipitated with ethanol and acetone. The absorption peaks at 3237.46 cm^{-1} and 3344.15 cm^{-1}, as shown in Fig 1 (a) and 2 (a) respectively, indicate O-H stretching vibrations. This suggests the presence of hydroxyl groups, which are components of sugars such as galactose or rhamnose, as well as hydrogen bonds within the structure. The absorption peaks at 1606.81 cm^{-1} and 1603.57 cm^{-1} also support this observation. In Fig 1 (b) and 2 (b), the absorption peaks indicate C=O stretching (carboxylate group), which is a characteristic feature of galacturonic acid found in pectin, commonly present in okra. The absorption peaks at 1068.52 cm^{-1} and 1036.19 cm^{-1}, respectively, correspond to the most prominent and sharpest peaks related to the vibrations of C-O-C glycosidic bonds and C-O stretching. These are the main structural components of carbohydrates in the mucilage.

The IR absorption spectra shown in Fig 1 and 2 indicate that the extracted substance contains polysaccharides with carboxyl groups or pectin as the main components. This aligns with the chemical properties of mucilage from okra. According to the study by Jayraman (2016), the IR absorption range of green hibiscus mucilage is similar across all peaks.

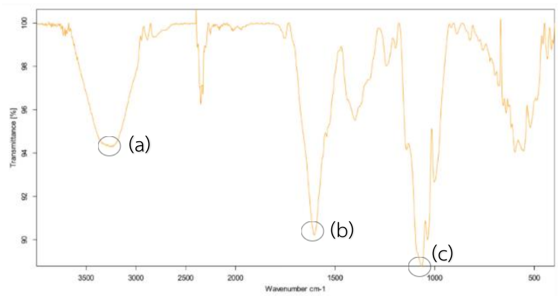

Fig. 1 A graph show IR absorption spectrum of mucilage precipitated with ethanol.

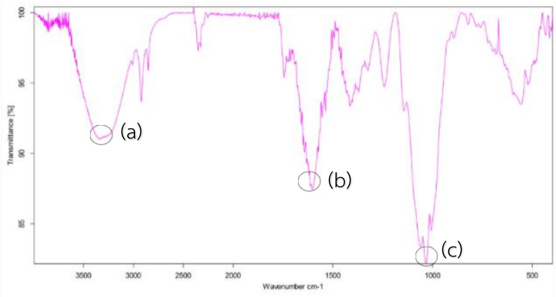

Fig. 2 A graph show IR absorption spectrum of mucilage precipitated with acetone.

1.2) The results of water holding capacity and pH of mucilage.

Table 1 show the mucilage extract from the okra, precipitated with ethanol and acetone, has water absorption capacities of 6.66 ± 2.00 g/g and 4.34 ± 0.55 g/g, respectively. The mucilage extract from okra precipitated with ethanol and acetone has pH values of 6.64 and 7.00, which are slightly acidic and neutral, respectively. These pH values are close to the study by Kannika Onsali (2018), which found that the pH of okra mucus was 7.52 ± 0.21.

Table 1 show water holding capacity and pH of mucilage

Type of precipitating agent	water holding capacity (g/g)	pH
Ethanol	6.66 ± 2.00	6.64
Acetone	4.34 ± 0.55	7.00

Part 2: Study of different ratios on the physical and chemical properties of hydrogels.

2.2) The results of the gel fraction and pH Values of hydrogel at different ratios.

Table 2 show the hydrogel at the ratio 0:0 has the highest gel fraction amount, which is 79.06 ± 0.38. The next highest are the hydrogels at ratios 2:1, 1:1, and 1:2, with values of 61.05 ± 9.42, 55.40 ± 2.62, and 45.42 ± 13.77, respectively. The pH values of the hydrogels at ratios 0:0, 1:1, 1:2, and 2:1 are 5.93, 5.18, 4.91, and 5.41 respectively.

Table 2 show gel fraction and pH Values of hydrogel at different ratios.

Zeolite:Humic Acid Ratio	gel fraction (%)	pH
0:0	79.06 ± 0.38	5.93
1:1	55.40 ± 2.62	5.18
1:2	45.42 ± 13.77	4.91
2:1	61.05 ± 9.42	5.41

2.3) The results of the liquid absorption capacity of hydrogel under free-swelling conditions at different ratios.

Table 3 shows that the hydrogel at ratio 0 : 0 absorbed the most liquid under free conditions: 10, 20, 30, 40, and 50 minutes, with values of 4.81, 6.80, 8.86, 9.54, and 10.62 g/g. The 1:1 ratio hydrogel absorbed 3.46, 4.94, 5.90, 6.94, and 7.53 g/g; the 1:2 ratio absorbed 3.55, 4.62, 5.21, 5.59, and 6.15 g/g; and the 2:1 ratio absorbed 6.61, 9.95, 11.25, 15.29, and 15.83 g/g at the same time points. The liquid absorption capacity of all hydrogels increased with longer soaking times, consistent with previous studies by Rakitikul (2020).

Table 3 show liquid absorption capacity of hydrogel under free-swelling conditions at different ratios.

Zeolite:Humic Acid Ratio	liquid absorption capacity of hydrogel under free-swelling conditions (g/g)				
	10 Min	20 Min	30 Min	40 Min	50 Min
0:0	4.81	6.80	8.86	9.54	10.62
1:1	3.46	4.94	5.90	6.94	7.53
1:2	3.55	4.62	5.21	5.59	6.15
2:1	6.61	9.95	11.25	15.29	15.83

Part 3: Fertilizer release test of hydrogel synthesized from mucilage of okra at different ratios.

3.1) The results of the change in sample weight every 2 days over a period of 12 days.

Table 4 show the sample weights changed every 2 days over 12 days. All hydrogels, fertilizers, and water-absorbing polymers showed weight loss over time.

Table 4 show the change in sample weight every 2 days over a period of 12 days.

Zeolite:Humic Acid Ratio	Hydrogel weight every 2 days (g)						
	Before soil application	2	4	6	8	10	12
0:0	1.82 ± 0.25	1.19 ± 0.16	0.63 ± 0.06	0.51 ± 0.02	0.48 ± 0.01	0.45 ± 0.01	0.34 ± 0.03
1:1	0.95 ± 0.2	0.8 ± 0.1	0.75 ± 0.09	0.58 ± 0.04	0.48 ± 0.02	0.36 ± 0.03	0.26 ± 0.02
1:2	0.92 ± 0.17	0.78 ± 0.03	0.51 ± 0.08	0.46 ± 0.04	0.37 ± 0.02	0.29 ± 0.03	0.23 ± 0.03
2:1	0.87 ± 0.04	0.83 ± 0.04	0.77 ± 0.02	0.58 ± 0.05	0.51 ± 0.02	0.47 ± 0.02	0.42 ± 0.04
fertilizer	0.25 ± 0	0.18 ± 0	0.11 ± 0.01	0.08 ± 0.01	0.07 ± 0.02	0.06 ± 0.01	0
water-retentive polymers	2.36 ± 0.23	1.6 ± 0	1.52 ± 0.02	1.31 ± 0.24	1.17 ± 0.22	1 ± 0.04	0.96 ± 0.01

3.2) The results of N, P, K contain in soil after nutrient release from hydrogel.

Table 5 shows nutrient (N, P, K) release in soil over 12 days, increasing with time across treatments: water-retentive polymers, fertilizer, and hydrogels at ratios 0:0, 1:1, 1:2, 2:1.

Table 5 shows N, P, K contain in soil after nutrient release from hydrogel

Zeolite:Humic Acid Ratio	ปริมาณธาตุอาหาร (g/100g)								
	N			P			K		
	4	8	12	4	8	12	4	8	12
0:0	0.44	0.48	0.49	0.16	0.31	0.34	0.19	0.38	0.48
1:1	0.45	0.47	0.49	0.22	0.27	0.40	0.30	0.39	0.47
1:2	0.46	0.48	0.50	0.23	0.26	0.30	0.29	0.31	0.46
2:1	0.43	0.45	0.47	0.22	0.25	0.29	0.28	0.32	0.45
fertilizer	0.47	0.49	0.52	0.23	0.38	0.43	0.30	0.45	0.51
water-retentive polymers	0.36	0.38	0.42	0.21	0.26	0.31	0.23	0.31	0.36

Conclusions

1) The chemical structure analysis of the mucilage extract from Hibiscus sabdariffa was performed using ATR-FTIR with ethanol and acetone extraction methods. The absorption ranges of the main functional groups showed similar peak positions and characteristics, indicating that the substances obtained from both methods are indeed mucilage from Hibiscus sabdariffa.

2) The mucilage extract precipitated with ethanol has a higher water retention capacity and acidity compared to the extract precipitated with acetone.

3) The ratio 0:0 produced the highest gel structure and pH value, followed by ratios 2:1, 1:1, and 1:2, respectively.

4) The ratio 2:1 demonstrated the best liquid absorption ability across all time points, followed by ratios 0:0, 1:1, and 1:2, respectively.

5) The ratios 0:0 and 2:1 showed a gradual change in average weight. On day 12, the 2:1 ratio had the highest average weight, followed by 0:0, 1:1, and 1:2. The 1:2 ratio showed rapid weight changes. Compared to conventional chemical fertilizers, which degrade quickly, and commercial water-retaining polymers, which have

high weight and gradual weight change, the mucilage-based formulations exhibit different behaviors.

6) The ratio of zeolite to humic acid at 2:1 had the best capacity for slow nutrient release, while the ratio 1:2 released nutrients more rapidly.

Acknowledgments

This project was successfully completed with the invaluable guidance and support of many. We sincerely thank to Miss Jinda Ponatha and Miss Thanyanee Chokkanjanakul, our advisors, for their expert advice, meticulous guidance, and encouragement throughout this journey. We extend our heartfelt gratitude to the school administrators, educators, and every staff of Princess Chulabhorn Science High School Mukdahan, for their generous financial support, assistance with printing materials, and the use of facilities.

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