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A Practical Case Report on the Node Point of a Butterfly Model Circular Economy: Synthesis of a New Hybrid Mineral-Hydrothermal Fertilizer for Rice Cropping

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Abstract: With the increased importance of a circular economy in the world, in this paper we present a practical "butterfly model" (proposed by the Ellen MacArthur Foundation) case report: to gain extra benefits in rice cropping through hybridizing green products of mineral waste and agricultural waste recycling. Hydrothermal biorefinery was used to turn spent agricultural biomass into a value-added biomass nutrient solution (BNS). BNS and sericite mineral waste were mixed and used as a new hybrid mineral—hydrothermal fertilizer for rice cropping. The most important extra benefit of this new hybrid mineral—hydrothermal fertilizer was that the empty grains could be reduced to 1–4 grains/spike (normally, it is 12–18 grains/spike), without significantly decreasing the panicle weight or spike saturation. This case report provides a new logic for circular design at the "node" point of a butterfly diagram.

Keywords: butterfly model; circular economy; agricultural waste; mineral waste

1. Introduction

With a worsening solid waste problem, reducing agricultural and mineral waste through circular designs is now a rising trend [1]. The Ellen MacArthur Foundation has proposed a butterfly model for a circular economy. Recycling and reusing waste from household, industrial, and agricultural sources and returning waste to its own original application area in a closed-loop system has been practiced for a long time. In this paper, we present a practical case report at the node point of the "butterfly model". With consideration of the safety of waste, we demonstrate a case on the laboratory scale for crossing systems to gain extra benefits in rice cropping through hybridizing green products of mineral waste and agricultural waste recycling.

Agricultural waste output is approximately 4 million tons every year in Taiwan [2]. The composition of this waste (sugarcane exocarp, peanut shells, and rice husks) is lignocelluloses, cellulose, hemicelluloses, and lignin. In recent years, most agricultural biomass research has concentrated on a single type of lignocelluloses [3–7], for example, in applications to prepare high-strength ecological materials, soil improvers, and graphene-containing carbon materials [8,9]. These lignocelluloses' structures do not easily break up and require chemical or physical degradation. If this biomass is burned, then it becomes a source of environmental pollution. Using high temperature or pressure does not require the addition of chemicals or requires only the addition of non-toxic chemicals that can be recycled, resulting in reduced environmental pollution [10].

Sericite is one of the most commonly altered minerals from the hydrothermal ore-forming process. It is a rich and low-cost material widely used in thermoplastics, cosmetics, food packaging, toys, and

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automobile coatings [11,12]. In recent years, sericite has been the focus of many scholars' attention as an electric insulator [13], in its use for improving the adsorption of strontium [14–18], and for its ability to remove cesium, copper, lead, cadmium, phenol, and nickel heavy metal ions [19].

Sericite and agricultural waste contain silicon (Si) and potassium (K); they could be used in soil to enhance the stress tolerance of a wide variety of crops, as they could greatly boost rice yield and mitigate abiotic stress, especially from a drought [20]. Research results have confirmed that, under saline conditions, silicon could prove to be a better strategy for maintaining crop productivity [21–25]. The addition of Si fertilizer can alleviate K-deficiency-induced growth inhibition by improving the plant's water status via enhancement of stomatal conductance and transpiration rates such as number of grains per panicle, seed-setting rate, and 1000-grain weight [3]. In summary, the beneficial effect of silicon applied to soil or as a foliar application has been well recognized.

In recent years, the decline in rice yields as a result of excessive chemical fertilizer (CF) inputs is a matter of great concern in rice-growing regions of Asia [26]. Subtropical and tropical soils are generally low in available Si [27]. Heavy metal pollution in paddy soil also results in retardation and yield losses [28]. Therefore, from the viewpoint of circular design for agriculture, we can consider the application of silicon-containing mineral waste such as sericite to promote crop growth. This study used a cellulosic biomass nutrient solution (BNS) made from the hydrothermal carbonization (HC) of agricultural waste, as described in our previous investigations [29,30], and sericite mineral waste to enhance rice growth by reducing empty grains.

2. Experimental Section

2.1. Sample Preparation and Characterization

The agricultural waste biomass (sugarcane exocarp, peanut shells and rice husks) was crushed separately and mixed equally in a ratio of 1:1:1 (100 g each, total was 300 g). This was used to create the BNS in a 6.0 L hydrothermal carbonization reactor at 200 $^{\circ}$ C and 15 atm for 1 h.

Sericite powder was provided by the manufacturer. Peanut shells, sugarcane exocarp, and rice husks were obtained from a farm in Tainan city (Taiwan). The morphology and chemical composition of the powder samples were analyzed using a scanning electron microscope (SEM, JSM-6700F, Japan) and energy dispersive spectrometers (EDX, S-3000N, HITACHI, Japan). Soil phase and heavy metal analysis by ion coupled plasma spectrometry(ICP) were used to characterize the chemical composition of the BNS liquid.

2.2. Rice Growth Experiments

In the rice growth experiment, rice seeds were planted in plastic pots in the net-house of a laboratory at the campus of National Pingtung University of Science and Technology (NPUST, DMS: 22°38′27″ N, 120°35′44″ E), and different fertilizers were applied after seeding for one season (March 5, 2017 to July 5, 2017). The different fertilizers used in the rice growth experiment were set as: a control group for water (*Ck*), sericite (*EX1*), BNS (*EX2*), and a BNS/sericite mixture (*EX3*), which was based on the experiment being a comparison of the effects of different additives on rice.

Rice seed (Taiwan Terrier No. 9, the most popular applied species) was obtained from farmers. The details of rice cropping are described in the following, for example: In one pot, five rice seeds were used. A volume of 100 mL of the BNS was mixed with 40 and 30 g of sericite, respectively, and then 30 g of pure water was prepared for draining. Finally, 21.6 kg of soil was placed into test pots, each pot having a length of 40 cm, a width of 36 cm, and a height of 15 cm. After planting, groundwater was applied into the pots up to 1 kg higher than the soil. The experimental combinations included: (1) (Ck) 30% water + 21.6 kg soil, (2) (EX1) 30% sericite + 21.6 kg soil, (3) (EX2) 40% BNS + 21.6 kg soil, and (4) (EX3) 40% BNS + 30% sericite + 21.6 kg soil.

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The rice growth data were observed and recorded (Figure 1) every 10, 20, and 30 d before harvesting, during which time rice samples were taken to measure the plant height, spike height, grain number, empty envelopes, saturation, panicle weight, grain weight, and empty grains.

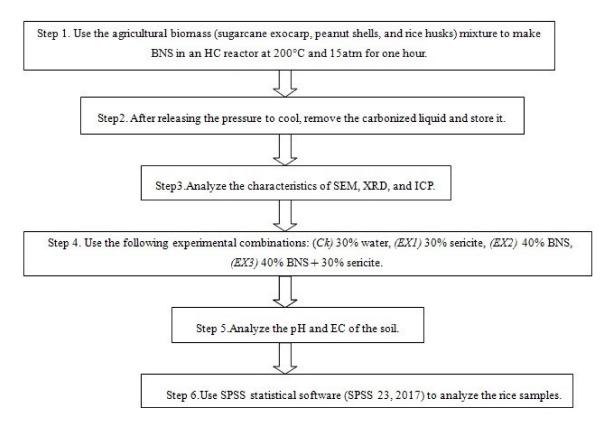


Figure 1. Experimental flow diagram.

3. Results and Discussion

Table 1 shows the EDX analysis data of the sugarcane exocarp, peanut shells, and rice husks used as the raw materials for the BNS. Results show that the sugarcane contained 52.64% C and 0.8% Si, the rice husk contained 32.41% C and 19.71% Si, and the peanut shells contained 43.78% K and 1.91% Si (Table 1). The EDX analysis (Table 2) of the sericite showed that it contained 0.48% Mg, 17.67% Al, 23.24% Si, 6.57% K, 0.2% Ca, and 1.46% Fe. The content of the solid sericite was mainly composed of 23.24% Si and 17.8% Al. The soil had a high Si/Al ratio and a high Si/Fe ratio, indicating that the plants could absorb more Si from the soil [30,31]. Figure 2 shows that the dry sericite powder had a lamellar structure with irregular vertical overlapping; the magnification of photos is about x100. Table 3 shows the calculated elemental compositions of the new synthesized fertilizer.

Table 1. Elemental compositions of sugarcane exocarp, peanut shells, and rice husks from energy-dispersive spectrometer (EDX) analysis.

Element	С	0	Si	N	K	Ca	Al	Ni	Cl	Mg
Sugarcane exocarp, raw	52.64	46.56	0.80	ND						
Peanut shells, raw	43.78	44.69	1.91	0.92	2.75	1.82	0.56	ND	1.66	1.91
Rice husks, raw	32.41	46.84	19.71	0.06	0.66	0.66	ND	ND	ND	0.06
Sugarcane (BNS)	57.00	41.70	2.00	0.25	ND	0.05	ND	ND	ND	ND
Peanut shells (BNS)	62.04	33.58	2.17	0.23	0.18	0.57	1.02	ND	ND	0.21
Rice husks (BNS)	50.79	43.51	4.09	ND	ND	0.03	ND	1.58	ND	ND
Equally mixed BNS	56.60	39.60	2.75	0.16	0.06	0.22	0.34	0.53	ND	0.07

Unit: wt%; ND means "Not detectable".

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Element	0	Na	Mg	Al	Si	K	Ca	F
#1	49.46	0.9	0.52	17.81	23.43	6.52	0	1.36
#2	49.84	0.6	0.44	17.52	23.04	6.61	0.4	1.55
Averaged	49.65	0.75	0.48	17.67	23.24	6.57	0.20	1.46

Table 2. Elemental compositions of sericite from EDX analysis.

Unit: wt%.

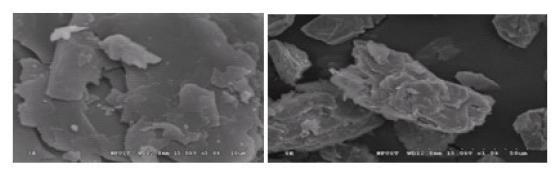


Figure 2. Scanning electron microscope (SEM) images of sericite.

Table 3. Elemental compositions of the new synthesized fertilizer.

Element	C	O	N	K	Si	Al	Ca	Mg	Na	Ni	F
40% BNS + 30% sericite	22.64	30.74	0.06	0.02	8.07	5.44	0.15	0.03	0.23	0.21	0.44

Data calculation from Table 1; Table 2. Unit: wt%.

The pH and electro-conductivity (EC) of the BNS are 7.0 and 3.5 us/cm, respectively. The ICP element analysis (Table 1) revealed that the sugarcane contained 15.37% K, the rice husk contained 53.28% K, and the peanut shells contained 97.14% K, with high contents of C and Si [29,30]. Figure 3 shows that the addition of BNS and sericite increased rice plant height, number of grains, and panicle weight when compared with Ck (pure water only). The experimental results showed that, with the use of BNS and sericite, the rice plants had better growth performance than the control group (pure water only): (1) the rice plant height increment was 52.4 cm, increasing from 68.6 to 121 cm, and the degree of saturation rose by 3.9%, (2) the panicle weight increased by 1.65 g/spike. It can be seen from the above results that the application of BNS in the cultivation process of rice can not only increase the plant toughness and resistance to pests and diseases, but can also increase the yield of rice and produce high-quality rice to improve economic benefits.

Figure 3 and Table 4 show the relationship between plant height and empty envelope of grain with the application of the new hybrid fertilizer. The rice plants grown using BNS and sericite are higher than the control group. The plant height of the rice increased amount by 52.5 cm, and the empty envelope of grain increased by 12.9%. The application of the new hybrid fertilizer affects the plant height and empty envelope of grains. The rice plant height and seed setting rate are positively correlated.

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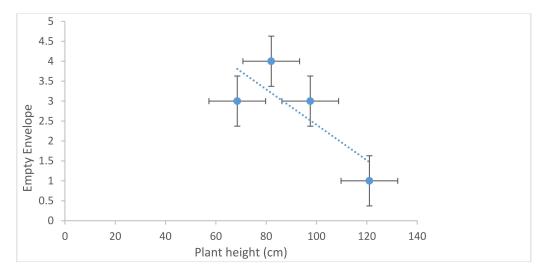


Figure 3. Relationship between plant height and empty envelope of grain: new hybrid fertilizer.

Elemen	nt Plant Height (cm)	Spike Height (cm)	Empty Envelope of Grain (grain/spike)	Saturation of Spike (%)	Seed Setting Rate (%)	Panicle Weight of Grain (g/spike)
1. (Ck) (30% Water)	68.6	11.5	3	62	95.4	3.6
2. (EX1) 30% Sericite	97.6	12.5	3	122	97.6	4.3
3. (EX2) 40% BNS	82.0	13.5	4	112	96.6	3.8
4. (EX3) 40% BNS + 30%	121.0	17.5	1	135	99.3	5.3

Table 4. Effects of different additives on the rice experiment.

The most important impact of this study is that we observed that when the compound fertilizer and organic fertilizer were applied, the rice growth had a very high level of empty grains, accounting for 13–21 grains/spike, and the panicle weight was 4.2–5.8 g/spike [32–34]. Although the level of empty grains may be affected by rice variety, any correlation to growth condition is not considered here. From the results, we reduced the empty grains to 1–4 grains/spike when applying the new hybrid mineral–hydrothermal fertilizer without significantly decreasing panicle weight (3.8–5.2 g/spike) or spike saturation (110–130%). Because SPSS statistics software was not used, these experimental results need to be statistically validated. This case study shows promise at a very rudimentary level; however, further extensive studies are needed to confirm the repeatability of the results reported in this article.

4. Conclusions

This case report provides a new logic for circular design at the "node" point of a butterfly diagram of the circular economy proposed by the Ellen MacArthur Foundation. The Results and Discussion section in this paper is focused on the demonstration of a practical case for a circular economy; this section is not focused on the mechanism or causal factors of plant growth. Therefore, the case study indicates promising results but needs further validation with repeated experiments that can be statistically validated.

An additional future implication is how to create larger markets; this is still a big problem due to the fact that the use of recycled materials is related not only to a scientific technique, but also to the willingness of potential consumers. Cross-system matter circulation is our goal; it can address the issue of personal willingness, but it also needs a demonstration of the process from practical cases, social-benefit sand-box building, and official legislation.

Data Availability Statement: All data, models, and code generated or used during the study appear in the submitted article.

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