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Waste to Value through Rice Hull to Nano-silica: A Novel Paradigm of Sustainable Agronomy

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***Abstract* — Although Silicon (Si) in its bulk phases has long been used as a fertilizer in agriculture, specifically for those in the Poaceae family, the unique role their nanoscale counterparts may adopt in modern day agriculture remains mostly unknown. *Oryza sativa* (rice) is among the main agricultural crops in Sri Lanka. The rice plants accumulate and greatly benefit from Si, where it is deposited beneath the cuticle as cuticle-Si double layer in the form of silicic acid. Further, Si may also interact favorably with other applied nutrients, hence improving the agronomic performance, crop yield, as well as the tolerance of rice plants to abiotic and biotic stresses, thus making Si essential in sustainable rice production. The hull, or the hard protective layer of the rice grain, is mostly regarded as a bulk-scale waste produced during the post-harvest processing of rice. Nevertheless, it is notable that Si is a prominent constituent in rice hull. Hence, there have been recent attempts to utilize rice hull as a precursor for producing Si nanoparticles. However, such approaches, still being in their infancy, requires further systematic investigations to optimize the nanoparticle preparation, in terms of the ensuing nanoparticle properties (i.e., size, morphology, and porosity etc.) as well as the process economies themselves. Hence, in this study, a novel, facile, efficient, and scalable strategy was systematically developed for the preparation of Si nanoparticles from waste rice hull. Notably, pre-processing conditions, synthetic parameters, and the chemical usages were optimized to allow scalability and sustainability to ensue. Initial characterization of the nanoparticles synthesized under aptly optimized conditions indicated the ability of this novel approach to synthesize nanoparticles of smaller dimension that could be stably suspended in aqueous media for prolonged durations without any signs of instability. Further investigations are ongoing in terms of creating and controlling the porosity of these nanomaterials, which will further enhance their carrier properties and thus the applicability as an effective nano-fertilizer. Overall, the knowledge imparted by this study will be significant in intensifying agricultural practices, specifically in many developing parts of the world, where rice remains to be a prominent crop, thus indicating a novel paradigm of sustainable agronomy.**

Keywords* — *Rice hull, Nano-silica, Synthesis, Stability, Nano-fertilizer

I. INTRODUCTION

Mineral nutrition is well known to contribute towards improving the quality and yield of cereal crops. Silicon; a quasi-essential element abundant in many soils has proven to be effective in producing (1) increased resistance to pathogens and insects, (2) increased resistance to strong wind and rain, (3) reduced lodging, (4) enhanced uptake of K, P and Ca, as well as (5) the alleviation of P deficiency, drought stress, salt stress, and metal toxicity (Mn, Cd, As, Al, Zn, Fe etc).[1]–[3] However, the ability of bulk Si to produce the above effects would depend on their transport through the plant. Hence, it is intuitive to believe that if Si in nanoscale is incorporated into fertilizer applications, the transport process will be momentously enhanced, thereby greatly amplifying the above benefits.[4]

Additionally, with the recent advent of nanotechnology, it is well-known that matter may adopt unique properties, specifically, some of which might even be significantly different from those in the bulk-scale, due to the distinctive quantum confinement effects that prevails in the nanometer regime.[5], [6] As a result, some materials have been found to produce novel properties, specifically resulting from their nanoscale dimensions. Scientific research in this regard is mostly ongoing, and of note, some recent findings have proven that nanoparticles of Si or nano-silica are a powerful and versatile tool that is greatly underutilized in contemporary agriculture, where the anticipated unique benefits may include (1) enhanced regulation of plant growth, (2) enhanced resistance to environmental stress, (3) significant improvement in soil quality (mainly the water holding capacity), and (4) the ability to serve as potential carries for fertilizers, pesticides, herbicides, or even DNA and proteins.[1]–[3]

Oryza sativa (rice) is among the main agricultural crops in Sri Lanka. The rice plants accumulate and greatly benefit from Si, where it is deposited beneath the cuticle as cuticle-Si double layer in the form of silicic acid.[7] Further, Si may interact favorably with other applied nutrients, hence improving the agronomic performance, crop yield, as well as the tolerance of rice plants to abiotic and biotic stresses, thus making Si essential in sustainable rice production.[8] However, the effect of this imperative nutrient in rice cultivation at the nanoscale has not been explored thus far.

The hull, or the hard protective layer of the rice grain, is mostly regarded as a bulk-scale waste produced during the post-harvest processing of rice. Nevertheless, it is notable that Si is a prominent constituent in rice hull.[7] Hence, there have been recent attempts to utilize rice hull as a precursor for the production of Si nanoparticles.[9]–[11] However, such approaches, still being in their infancy, requires further systematic investigations to optimize the nanoparticle preparation, in terms of the ensuing nanoparticle properties (i.e. size, morphology, and porosity etc) as well as the process economies themselves. Notably, if novel, facile, efficient, and scalable strategies could be developed for the preparation of Si nanoparticles from the waste rice hull, and the ensuing shape size and concentration effect of the same in rice cultivation is systematically evaluated, the knowledge acquired would be greatly significant in intensifying agricultural practices, specifically in many developing parts of the world, where rice remains to be a prominent crop.

II. OBJECTIVES

The focus of this study was to develop a novel method to effectively prepare Si nanoparticles using rice hull as the Si precursor, and to assess the effect of the same in rice cultivation. Notably, the initial investigations have revealed that nano silica synthesized under aptly optimized conditions indicated the ability of this novel approach to synthesize nanoparticles of smaller dimension that could be stably suspended in aqueous media for prolonged durations without any signs of instability.

III. METHODOLOGY

Synthesis of nano-silica: Synthesis of nano-silica was conducted using a modified procedure based on methods previously reported in literature.[12]–[14] First, the rice hull (RH) was cleaned with tap water and deionized water, dried in an oven. Then, it was soaked in 1 M hydrochloric acid (HCl) for 2 hours, washed with deionized water and dried in an oven again. The as-prepared RH was sintered in a muffle furnace at a standard temperature and time to obtain rice hull ash (RHA). Then, RHA was ground into a powder, which was washed again with HCl by mixing for 2 hours followed by overnight soaking. Then, the solution was centrifuged, and the supernatant was replaced with deionized water until any excess acid is removed, as confirmed with the help of pH papers. Then, a standard solution of sodium hydroxide (NaOH) was added into the RHA and the solution was heated while stirring until the ash was completely dissolved, followed by hot filtration. Once the filtrate was cooled to room temperature, a known volume of deionized water was added to the solution and finally a standard solution of sulfuric acid (H_2SO_4) was added dropwise under continuous stirring until the solution was completely neutralized and a turbidity was observed. The as-synthesized particles were purified via repeated centrifugation followed by resuspension in deionized water. The cloudy suspensions obtained were transferred into reagent bottles and stored until further use. Above procedure was repeated multiple times to ensure repeatability of the procedure.

Optimization of synthetic parameters: In optimizing the scalability and the economic viability of the procedure developed for synthesizing nano-silica, (1) the need for acid washing, (2) reusability of the acid wash solution, and (3) the stability of the nanoparticles based on diluent volume used during the synthesis were optimized here. The above parameters were decided based on the cost-factors that would likely be associated in commercializing the scientific findings and the stability of the nanoparticles which is deemed to alter the behavior of the nanomaterials upon eventual application. The effect of acid washing on the synthesis of nano-silica was evaluated by conducting the above outlined synthesis procedure with and without the acid washing step, while all other conditions and parameters were held constant. The reusability of the acid solution for washing RH was evaluated by repeating the above outlined synthesis procedure with RH washed with fresh and used acid solutions, while all other conditions and parameters were held constant. The effect of diluent volume on the ensuing stability of the nano-silica was evaluated by repeating the above outlined synthesis procedure with different volumes of deionized water (50, 100, and 150 mL) being used as the diluent, while all other conditions and parameters were held constant.

IV. RESULTS AND DISCUSSION

All synthesis and analysis conducted here were done using RH obtained during the processing of a single batch of samba rice, while the pre-cleaned RH was mixed to ensure homogeneity within the sample. It was observed that the synthetic approach developed here could produce a fine aqueous suspension of nano-silica which could be stably suspended for prolonged durations. Hence, in optimizing the synthetic parameters further, the effect of acid washing, reusability of the acid solution for washing, and effect of diluent volume were systematically evaluated to understand their role in the synthesis process and/or in dictating the properties of the ensuing nanoparticles.

Figure 1 (A) shows an image of RH after acid-washing and drying. To evaluate the effect of acid washing, multiple samples prepared in this manner was sintered after being treated with concentrated acid, while control samples were used as is. Images of RHA obtained for the acid washed and unwashed RH are indicated in Figure 1 (B) and (C) respectively. As can be clearly seen, the acid washing was essential in (1) allowing complete combustion taking place during the sintering process, while (2) assisting the disintegration of the RH structure during sintering; both of which are important for the efficient pre-synthetic processing of RH. Clearly, for the controls where acid-washing was not conducted, incomplete combustion was observed as clearly visible by the appearance of the sintered samples, while the ensuing disintegration of the RH structure during the sintering was also minimal. Hence, it was inferred that acid-washing is essential to remove any impurities that are likely present in RH thus leading to incomplete combustion, while the same assists the efficient disintegration of the carbonaceous backbone of RH during sintering.

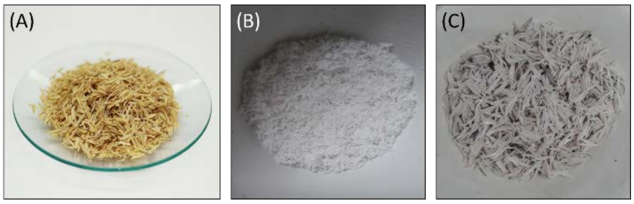

Fig. 1. Images of (A) acid-washed and dried RH, and RHA (i.e. sintered RH) (B) with and (C) without acid washing

As per the overall objective of developing a novel nano-fertilizer with silica, process scalability, economic viability, as well as environmental sustainability were considered as important considerations. Hence, to assess the reusability of the acid solution for washing RH experiments were conducted to observe RHA washed with fresh and reused acid solutions of a standard solution. Leaching of phytochemicals and/or impurities into the acid solution was clearly apparent after even after the first round of washing, hence indicating that the efficiency of the acid solution would decrease with successive use.

However, as observed by the images of RHA washed using fresh, twice, and thrice used acid solutions in Figure 2 (A), (B), and (C) respectively, efficient sintering was apparent with acid solutions reused up to three rounds of washing. All samples washed with acid solutions reused beyond this level indicated inefficient processing as was clearly apparent by the hue and the presence of blackish RH resides which were apparent post-sintering. Hence, in optimizing the reusability of the acid solution for washing RH during the pre-processing, it was inferred that the acid washing could be done with fresh, once-used, or even twice-used acid solutions without hampering the anticipated pre-processing of RH thereby assisting the economic viability as well as environmental sustainability of the synthetic approach developed herein.

Eventually, the RHA obtained in this manner was used in the nano-silica synthesis where the formation of nanoparticles was apparent by the appearance of a cloudy turbidity in the otherwise clear solution during the final neutralization step (Figure 2 (D)). However, it was apparent that the formation of nanoparticles was accompanied by the observation of a thick gel in the synthetic medium which is likely to hinder any successive nucleation and growth of nanoparticles that may ensue. Hence, to minimize this, dilution of the synthetic medium was conducted using deionized water right before the final acid addition step, thus allowing the solution viscosity to be remain intact during the nanoparticle formation. As anticipated, dilution of the synthetic medium led to the formation of nanoparticles as evidenced by the formation of a cloudy suspension upon neutralization, without any gel formation.

Fig. 2. Images of RHA washed using (A) fresh, (B) twice, and (C) thrice used acid, and (D) the milky suspension of ensuing nano-silica

Hence, to optimize the diluent (i.e. deionized water) volume used during the synthesis, the synthesis procedure was repeated with different volumes of deionized water being used as the diluent, while all other conditions and parameters were held constant. This indicated that the synthetic medium could be efficiently diluted with deionized water thereby diminishing any gel formation, while still leading to the formation of nanoparticles. However, further dilution of the medium indicated that nucleation may be hindered due to decreased precursor concentration hence dampening the nanoparticle formation. Thus, the experiment conducted here allowed to identify the optimum diluent volume to be used for the nano-silica synthesis.

The nanoparticles prepared in this manner indicated significantly stable dispersion stability where no signs of precipitation were apparent for prolonged durations of up to few months. Further, in the absence of microscopic characterization, the appearance of the suspension as well as the prolonged suspension stability serves as evidence for the smaller dimensions of the nanoparticles formed via this novel synthetic approach. Nevertheless, such dispersion stability is deemed important in utilizing the nanoparticles in fertilizer applications where the suspensions could be directly applied onto a desired crop, while the stability and the smaller dimensions of the nanoparticles will increase the uptake as well as the nutrient delivery that the nanoparticle fertilizer is anticipated to perform.

Further detailed characterization of the nanoparticles developed here, and the investigation of their fertilizing efficacy are ongoing. However, with the initial observations reported here, the study will likely result in a process by which rice hull could be efficiently transformed into an effective and sustainable fertilizer starting with waste rice hull, indicating competent use of technology in facilitating sustainable agricultural practices.

V. CONCLUSION

A novel, facile, and controlled synthetic approach was developed for the RH mediated preparation of nano-silica. The salient process parameters such as acid washing, reusability of acid was solution, as well as diluent volume were aptly investigated and systematically optimized via carefully designed investigations. Overall, the nano-silica obtained via the optimized synthetic pathway indicated exceptional dispersion stability, serving as initial evidence for the smaller dimensions as well as the appreciable stability of the nanoparticles produced here. Thus, the initial investigations conducted suggests that the process developed here is facile, scalable, and controllable in producing nano-silica that may efficiently be incorporated as a novel nano-fertilizer for the many crops that essentially requires silicon as a notable micronutrient. Investigations are ongoing in terms of creating and controlling the porosity of these nanomaterials, which will further enhance their carrier properties and thus the applicability as an effective nano-fertilizer. Overall, the knowledge imparted here is significant in intensifying agricultural practices, specifically in many developing parts of the world, where rice remains to be a prominent crop, while unfortunately RH is considered only as mere agricultural waste, thus indicating a novel paradigm of sustainable agronomy.

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