Research on Phosphorylation of Rice Husk – Used to Keep Moisturizer and Provided Nutrients for Plants

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***Abstract*—Rice husks are plentiful, as a potential source of nutrients. Rice husks have a rich chemical composition as cellulose, protein, micronutrients, especially organic silica, organic NPK. Rice husk is hydrolyzed by phosphoric acid solution to form the shorted cellulose. Rice husk hydrolysis efficiency is the best at phosphoric acid 59.06% concentration, reaction time in 2 hours with over 20% of the acid reactant. Products obtained the shorter cellulose components that have good water absorption of about 80g/g, biodegradable help plants absorb better. Increase the rate of germination 6-10%, the rate of height increase of 10-20% than controls**

Keywords—Rice husk, cellulose, nutrient

I. INTRODUCTION

Rice which is cultivated in more than 75 countries in the world is the essential food for over half the world's population. The worldwide annual rice husk output is about 80 million tones and over 97% of the husk is generated in the developing countries. Vietnam is an agricultural country with a very large annual rice production of over 40 million tonnes, followed by the release of about 7 million tonnes of rice husk. All of them are usually disposed by combustion or pour into canals causing serious environmental pollution. If without effective measures leading to problems environment and society.

Rice husk is known as a rich source of nutrients including: protein, amino acids, carbohydrate, micronutrients... especially organic silicon source, organic fertilizer (Nitrogen, phosphorous, potassium) is easy to penetrate [5]. The use of agricultural by-products reused in agriculture is a trend that the world is aiming to take advantage of available nutrients [1,2,5]. This study uses a hydrolysis of phosphoric acid (phosphorylation) [4] to produce a short-chain cellulose, protein, organic fertilizer, micronutrient, and organic silica... make the plants to absorb better

II. MATERIALS AND METHODS

A. Phosphorylation of rice husk

Husk husk washed, dried at 105^0C to constant weight, crushed. Treatment with Phosphoric acid solution with a ratio of 1g rice husk: 10ml H_3PO_4, stirring, soaking in two hours. Investigation of the effect of phosphoric acid concentration and reaction time on the hydrolysis of rice husk hydrolysis

- Effect of phosphoric acid concentration on the level of hydrolysis: Conducted with Phosphoric acid concentrations of 20-85%, with time reaction is about 2 hours. Analysis of acid concentration residue after reaction. To ensure the reproducibility of data, each experiment was conducted in triplicate and average of the three measurements was reported.

TABLE 1: Investigation of the effect of Phosphoric acid concentration on the level of hydrolysis

Phosphoric acid concentration (%)	20.44	30.72	40.17	48.93	59.06	67.73	82.05
Sample	ND2	ND3	ND4	ND5	ND6	ND7	ND8

Effect of the reaction time on the level of hydrolysis: Proceed with reaction time periods from 0-24 hours with the same initial phosphoric acid concentration. Analysis of acid concentration residue after reaction. To ensure the reproducibility of data, each experiment was conducted in triplicate and average of the three measurements was reported.

TABLE 2: Investigation of the effect of reaction time on the level of hydrolysis

Time (hour)	0	0.5	1	2	3	5	24
Sample	T0	T0.5	T1	T2	T3	T5	T24

B. Characterization of materials and products

The crystalline structure of MnO_2/Al_2O_3 catalyst was analyzed by X-ray diffraction (XRD) technique using a Bruker B8 Advance X-ray powder diffractometer. The elemental composition was determined by Energy dispersive analysis of X-rays (EDX, Varian Vista Ax). The thermo gravimetric analysis (TGA) was analyzed by 4.000 Mettler TA TGA

C. Survey the moisture retention of the material.

The moisture retention (MR) of the material (W_0, g), which was put into a tea-bag of nonwoven fabric, was immersed in water for different time periods (10, 20, 30, 40, 50, 60 minutes). The treated bag was allowed to hang on a holder for 10 minutes to separate the swollen sample (Ws, g) from the unabsorbed water. The experiment repeats 3 times. Degree of moisture retention was defined as follows:

$$MR\ (g/g) = (Ws-Wo)/\ Wo$$

D. Investigate the effect of material on soil moisture and plant growth

The experiment was conducted on maize (NK66), in greenhouse, covered roof, planted in pots. Each pots was germinated 3 seeds, watered fully, trimmed excess leaves only 1 plant per pot after germination. The experiments were arranged in complete randomized block, each formula (CT) was 3 times repeated, each replicate has 30 trees. Fixed the amount of 3kg of potting media and fertilizer are the same for each of the experiments, arranged with 3 experimental formulas:

CT1: Alluvial soil

CT2: 97% Alluvial soil + 3% sample T2

CT3: 95% Alluvial soil+ 5% sample T2

Monitoring of indicators: Soil moisture (%), germination time (day), germination percentage (%) was statistic at 10 days after sowing, plant height (cm) after 7, 14 and 30 sowing.

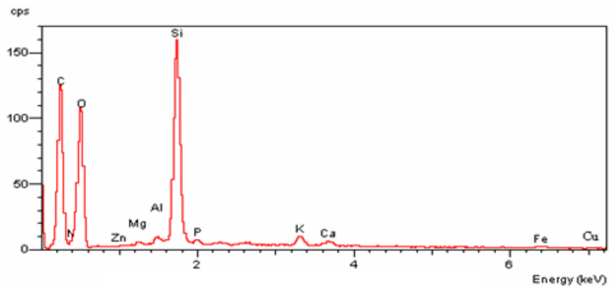

Figure 1. EDX diagram of rice husk samples

III. RESULTS AND DISCUSSION

A. Composition of elements in rice husk.

Rice husk are obtained in GiaLam district, HaNoi Capital, VietNam. The rice husk size: 8-12 mm length, 2.0-2.37 mm width and 0.1-0.15 mm thickness.

TABLE 3. Analysis of EDX rice husk samples.

Elements	C	O	Si	N	P	K	Zn	Cu	Mg	Fe	Ca	Al
Content (%)	42.19	35.54	11.96	0.4	0.9	8.03	0.45	0.15	0.12	0.14	0.07	0.05

In the composition of the rice husk contains a large of organic components, C 42.19%, that was mainly cellulose, in addition to the elements N, P, K, Si, Ca, Zn, Cu, Fe ... are essential nutrients for plant growth. The reuse of rice husk contributes to utilizing the available nutrients

B. Results of hydrolysis of rice husk with phosphoric acid.

- Effect of phosphoric acid concentration on rice husk hydrolysis.

TABLE 4. Effect of phosphoric acid concentration on rice husk hydrolysis.

Phosphoric acid concentration	ND2	ND3	ND4	ND5	ND6	ND7	ND8
C_0 (%)	20.44	30.72	40.17	48.93	59.06	67.73	82.05
C_f (%)	19.52	27.41	32.31	38.78	38.29	50.91	71.01
H_3PO_4 reaction (%)	0.92	3.31	7.86	10.15	20.77	16.82	11.04

** Reaction time: 2 hours*

Phosphoric acid is a weak inorganic acid, with a small acid concentration, hydrolysis is almost non-occurring, the best hydrolysis of about phosphoric acid concentration is 60%, with more than 20% of the acid involved in the process hydrolysis. When the concentration of phosphoric acid is higher, the hydrolysis process is slower because the phosphoric acid is viscous, reducing the mobility of the molecules involved in the reaction. Thus, the optimal concentration of phosphoric acid for hydrolysis process is about 60% for subsequent experiments

- Effect of reaction time on rice husk hydrolysis.

Investigation of the effect of reaction time on the hydrolysis of the rice husk showed that the first stage of hydrolysis was rapid. With the initial acid concentration is 59.06%, after 0.5 hour reactrion, the phosphoric acid concentration decreased to 46.22%.

TABLE 5. Effect of time reaction on rice husk hydrolysis.

Sample	T0	T05	T1	T2	T3	T5	T24
Time reaction (hour)	0	0.5	1	2	3	5	24
C_{H3PO4} (%)	59.06	46.22	42.67	38.97	38.35	38.18	38.12

During this period, phosphorylation occurs mainly in the amorphous part of the rice husk. Over time, the reaction is slowed down by the fact that in the crystalline region of the rice husk the structure of the spatial network is formed by the hydrogen bonds between the cellulose chains. At the same time, phosphoric acid is a weak inorganic acid so the phosphorylation of crystalline regions is very slow.

C. Characterization of materials

* Results of thermal gravimetric analysis (TGA) of rice husks and T2 samples.

On the rice husk hull thermal analysis diagram (a) there is a heat recovery peak at 128.12^{0}C corresponding to a mass reduction of 6.73%, which is the moisture removal process of the husk.

The thermal analysis diagram of the phosphorylation product -T2 sample (b) shows a structural dehydration at 118.51^{0}C corresponding to a mass loss of 21.31%. Thus, after phosphorylations, the product has a higher moisture content, higher water absorption capacity due to the phosphorylation formed the shorted cellulose molecules. Thermal decomposition of T2 sample was also smaller, indicating that the cellulose strength of the rice husk decreased [2].

- *EDX diagram of T2 sample.*

T2 samples- the product was formed by phosphorylation have good water absorption, as shown by the higher peak of oxygen intensity (oxygen accounts for about ~ 50%). The phosphorus content increased (1.7%) due to the phosphoric acid reacted with the cellulose chain in the rice husk to form ATP, ADP compounds [4].

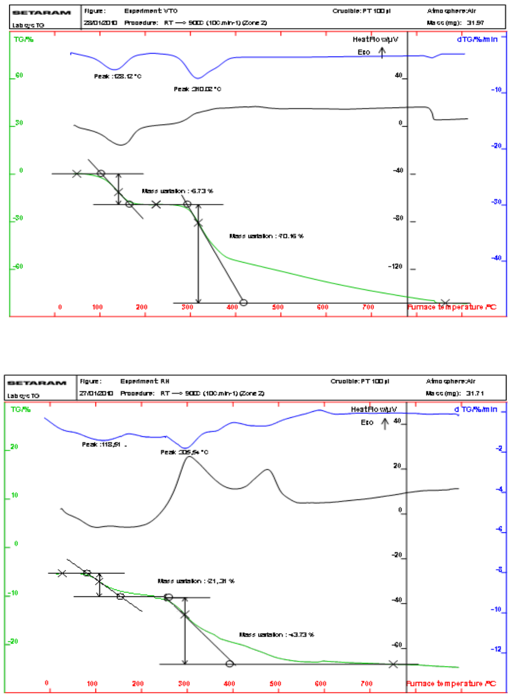

Figure 2. Schematic thermal analysis of samples of rice husk (a) and T2 sample (b).

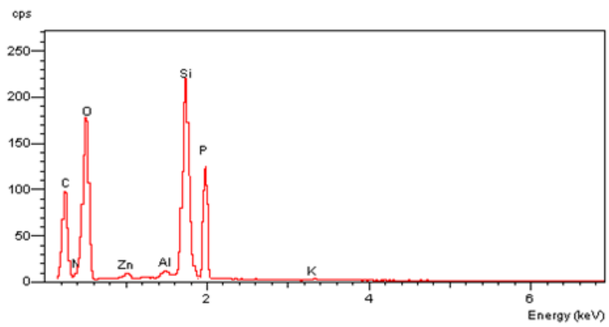

Figure 3. EDX diagram of the T2 rice husk sample.

- XRD diffraction of rice husk material and T2 sample

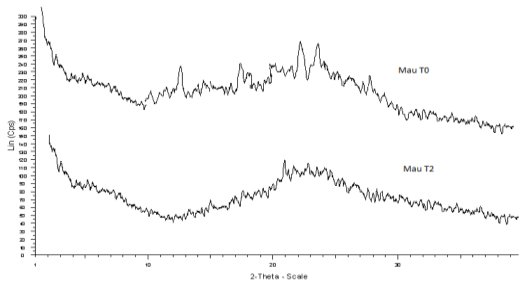

Figure 4. XRD diffraction of rice husk material and T2 sample

On the XRD diffraction pattern of rice husk material, the crystalline state of the cellulose were 2θ = 14.5; 16.7; 21; 22; 23; 24^0 were clear. On the XRD diffraction of T2 sample the degree of crystallization of the rice husk decreased significantly; the peaks characteristic of the crystalline state of the cellulose were 2θ = 14.5; 16.7; 21; 22; 23; 24^0 appeared with small intensity. It was shown that the husk was not completely hydrolyzed by phosphoric acid but only partially bound. Under the effect of phosphoric acid concentration 60%, the β-1,4-glycoside linkage in the cellulose was cut off, forming short chain amyloid components, reducing the crystal level of the cellulose. Pic at 2θ = 22^0 has a prison form that characterizes the amorphous state of silicon

D.Survey the moisture retention capacity of T2 sample

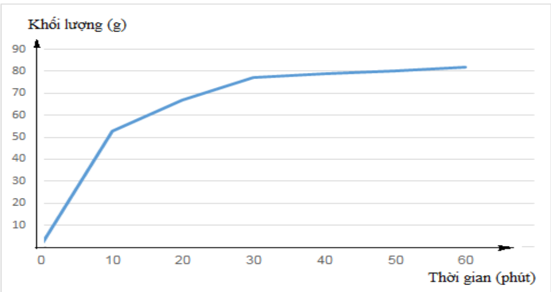

Figure 5. The moisture retention capacity of T2 sample

The moisture retention capacity of the T2 msample depends on the assay time. Initial water absorption occurs rapidly, then decreases over time to equilibrium. After approximately 30 minutes, water absorption is approximately 80 gram per gram T2 sample. As such, the T2 sample obtained has good moisturizing properties, which can be used to moisten the soil.

The good water retention of the T2 sample can be explained by the fact that the phosphorylation formed the short cellulose chain that can absorb and exchange high water. In addition, cellulose is characterized by the ability to swelling on phosphoric acid [4,5], which increases the swelling and moisture retention of the material.

E. Investigation of the effect of T2 on soil moisture and growth of maize NK66

During 30 days of planting, although irrigated with the same water and fertilizer regimen, the development of maize in the different treatments was uneven, depending on the amount of T2 material introduced into the soil.

Table 6. Investigation of the effect of T2 on growth of maize NK66

Parameters	Unit	CT1	CT2	CT3
Soil moisture	%	20.97	26.13	28.01
Germination time	day	5.8	4.6	4.1
Germination percentage	%	90.2	96.9	99.1
Plant height after 7 days	cm	10.01	12.71	13.88
Plant height after 14 days	cm	17.46	23.95	26.04
Plant height after 30 days	cm	78.05	90.23	95.81

In general, the results showed that the effect of T2 supplementation, germination time, germination percentage and plant height of the experimental plants increased significantly. Compared to the control samples (CT1), the samples were added T2 material (CT2, CT3) had shorter germination times than control samples, and higher germination percentage. Plant height growth also increased by 10-20% compared to control. This can be explained by the fact that samples with supplemented T2 sample are provided with appropriate moisture conditions that are suitable for seed germination. In addition, with the structure of shorted cellulose fibers forming holes, the holes increase the soil's porosity and help the roots to grow better and promote the growth of the plant. At the same time, the process of phosphorylation rice husk contributes to the formation of organic components, nutrients easily absorbed, and helps the plant propagate more favorably.

IV.CONCLUSIONS

The phosphorylation maked the rice husk chain was shorter to form amyloid compounds that facilitate the decomposition of rice husks by soil microorganisms. The flexible amyloid pulse is easy to expand collect a large amount of water, increase the ability of moisture and metabolism of rice husk. The T2 sample can be moisturizing absorbs about 80 gram per gram of water. Experimental investigations on the NK66 maize in green house showed that supplementing with moisturizing materials increased plant growth and development: reduced seed germination time, increased seed germination percentage, improved plant uptake and good metabolism of nutrients, height growth increased by 10-20% compared with control

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