



# Separation of some rice straw components and studying their effect on some hydro-physical properties of two different soils

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## ARTICLE INFO

### Article history:

Received 18 April 2013

Received in revised form 21 June 2013

Accepted 10 July 2013

### Keywords:

Rice straw

Cellulose

Silica

Lignin

Sandy soil

Calcareous soil

## ABSTRACT

Recycling the rice straw (RS) have been carried out using a simple laboratory procedure for different application purposes mainly the soil conditioning. Cellulose, Silica and Lignin could be extracted in a single process in almost pure form that is suitable for many environmental and industrial purposes. The raw RS, straw carbonized ash (RA), extracted Cellulose, Silica and Lignin were characterized by thermogravimetric analysis (TGA), FT-IR and elemental analysis. The mentioned materials were studied as agricultural soil conditioners. They were added in different concentrations to two soil samples different in their properties. Bulk density (BD), total porosity (TP), water holding capacity (WHC), field capacity (FC) and hydraulic conductivity ( $K_{sat}$ ) were estimated as examples of the studied soil physical properties. An enhancement in the studied properties for the sandy non-calcareous soil sample has been observed. For the more saline calcareous soil sample, the additives nearly have no effect on most of the studied properties. Some interaction between the soil particles, the additive particles and/or the absorbed water and may be present. The studied material may be promising as sandy soil conditioners.

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## Introduction

Rice straw (RS) is the residue and the excess of production of rice that was not utilized. The waste discharged can cause environmental problems and a loss of natural resources. If the wastes can be utilized, they are no longer wastes but become new resources. The most traditional uses of rice by-products include straw and hull for energy (production of biogas through anaerobic digestion), animal feed, building materials and paper production. An attractive alternative to recycling such waste is the compost production through microbial activity which is then mixed with the rock phosphate and ammonium sulphate to be used as an organic fertilizer [1–4].

The carbohydrate components of the RS are hemi-cellulose (~31.6%), Cellulose (~38.3%) and Lignin (~11.8%). High Silica content in RS (9–14%) prohibits the economic use. Hemi-cellulose is a large group of polysaccharides comprises over 30% of the dry mater of the straw. Unlike Cellulose, which is a unique molecule differing only in the degree of polymerization and crystallinity; they are inhomogeneous fractions and defined as the alkali soluble material after the removal of the pectic substances. Most of their preparations are soluble in water after alkaline extraction [5]. Cellulose is a semi-crystalline linear biopolymer with ordered

crystalline and disordered amorphous regions. It is a  $\beta$ -(1 → 4)-linked polymer of D-glucopyranosyl units. It does not melt before thermal degradation because of strong intra- and intermolecular H-bonding. Cellulose-based super absorbent hydrogels have been prepared and used to enhance water retention in soil. Because of their excellent hydrophilic properties, high swelling ratio and biocompatibility, they can be used in agriculture, biomedical area and sorbents for the removal of heavy metals [2,6–9].

Lignin is a polymer of phenyl propane units, which form a three-dimensional network inside the cell wall and has associated with other polysaccharides. The major inter-unit linkage is an aryl–aryl ether type. Due to the H-bonds between the polysaccharides and the adhesion of Lignin to them, the RS with its complex structures is hard to be bio-degraded even by anaerobic microorganisms or degradation enzymes. Lignin contains a number of functional groups like phenolic, hydroxyl, carboxyl, benzyl, alcohol, methoxyl, aldehyde, etc., and it can bind heavy metal ions such as iron, copper and zinc. As a natural polymer it should be preferred as an organic soil amendment rather than other non-natural bio-solids. Lignocellulosic materials are converted to humic substances during the composting process. Various waste organic by-products including compost, manure and paper mill sludge have been used to improve soil quality by improving soil aggregation, increasing nutrient availability and microbial activity [7,10,11].

Among the RS related materials; is the ash as an inorganic constituent (~18.3%) containing up to 77% Silica. Rice plants cumulate Silica through polymerization of the water-soluble silicic

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acid ( $\text{H}_4\text{SiO}_4$ ) absorbed from soil into insoluble poly silicic acids, followed by precipitation as amorphous Silica and deposition in exterior plant cell walls. In this process, rice acts as a bio-refinery factory for high quality amorphous Silica. It could be obtained simply by burning RS in air at temperatures above  $450^\circ\text{C}$  [8,9,12].

Silica particles may include fine powder (sub-micrometre sized) or amorphous nano-sphere particles. A wide range of electronic applications include, thermal and electrical insulators, optoelectronic devices, ceramics, chromatography and in manufacturing of chemical mechanical polishing slurries (CMP) required in the semi-conductors industry. Silica nano-spheres have been prepared through dissolution–precipitation process from ash provided from a gas production unit of RS [13].

Rapid and accurate determination of the chemical composition of the RS is crucial to prediction of its value. Several studies have reported multi-step complicated and time consuming biological and chemical processes that can be used to isolate one or more of the components for different applications purposes [2,12,14]. Chemical modification to obtain some derivatives of improved thermal stability and mechanical properties had been carried out [15]. Utilization of one component often leads to disposal problems [11]. Organic solvents like dioxan and toluene, catalysts like sulphuric acid, high temperature up to  $130$  and  $180^\circ\text{C}$  [2,12], autoclave and mechanical, high pressure steam techniques were used to partially remove Lignin and hemicellulose for the isolation of Cellulose from RS. Silica often was un-dissolved in such processes but obtained by burning at  $550^\circ\text{C}$  and sometimes after alkaline treatment of the de-waxed straw and many evaporation/concentration steps [16,17]. Most of the associated Lignin was degraded in the photo-catalyzed straw to obtain a higher yield of Cellulose neglecting Silica [18–21].

In the present study, a simple single-step recycling process has to be developed in which the main RS components were separated. The separates obtained were then isolated, purified and characterized. The recycled RS products added to two types of agricultural soil to study their effect on some soil hydro-physical properties in order to evaluate the possibility of their use as agricultural soil conditioners.

## Materials and methods

### Materials

#### RS

It was supplied as agricultural wastes from the field at the harvest time. The dried straw was washed by distilled water to remove dust, oven-dried at  $70^\circ\text{C}$  for 10 h, and ground to pass through a  $0.4\text{ mm}$  sieve.  $\text{NaOH}$ ,  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}_2$  were Merck products.

#### Soils

Two agricultural disturbed soil samples: S1 and S2 (0–30 cm depth) were used for the study. They were obtained from two different locations in Egypt, El-Esmailyia and El-Nubaryia Agric. Res. Stations, respectively. Both samples were air-dried, ground, sieved with a  $2\text{ mm}$  sieve and kept for the study. Some of their

properties were measured according to Page et al. [22] and presented in Table 1. The S1 soil was calcareous sandy clay loam with a high content of the fine particles as fine sand, silt and clay and slightly higher concentration of soluble ions. The S2 soil was non-calcareous sand with a high content of coarse sand and lower content of soluble ions.

### Methods

#### Liquefaction of RS

50 g RS was added to 1000 mL of 15% aqueous  $\text{NaOH}$ . The mixture was mechanically stirred at  $85^\circ\text{C}$  for 2 h then filtered using Wattman filter paper no. 5. The residue (un-bleached Cellulose) was washed thoroughly by distilled water, oven-dried at  $40^\circ\text{C}$  and ground to pass through a  $0.4\text{ mm}$  sieve.

Hot dark brown filtrate was collected and cooled to room temperature. The pH of the filtrate (pH 12.6) was adjusted using conc.  $\text{H}_2\text{SO}_4$  ( $18.4\text{ M}$  – 98%) at pH 7–8 with continuous stirring. When precipitated Silica appeared in solution, stirring was stopped and the solution was left for 30 min till precipitate coagulate then filtered through filter paper. Silica separated by filtration was washed by distilled water then transferred to a porcelain crucible and thermally treated at  $550^\circ\text{C}$  in a muffle furnace for 1 h.

The pH of the remaining dark brown filtrate (pH 8) was adjusted at pH 2–3 by conc.  $\text{H}_2\text{SO}_4$  ( $18.4\text{ M}$  – 98%) to precipitate acid-insoluble Lignin which was filtered, washed by distilled water then air-dried. Its dark brown colour turned black.

A 5 g of the un-bleached Cellulose was bleached by stirring at  $45^\circ\text{C}$  for 3 h in a 100 mL 15% aqueous  $\text{H}_2\text{O}_2$  (pH 9.9). The mixture was then filtered and the residue was washed thoroughly by distilled water, oven-dried at  $105^\circ\text{C}$  for 2 h (final weight  $3.7933\text{ g} \approx 75.87\%$ ).

A 10 g of RS was ignited at  $550^\circ\text{C}$  for 10 min to obtain the carbonized (RA) ( $1.722\text{ g} \approx 17.22\%$  carbonized powder).

#### Instrumental characterization

RS and its different extracted fractions: the RA, the un-bleached Cellulose, bleached Cellulose, Silica and acid-insoluble Lignin were characterized by thermo-gravimetric analysis (TGA) using Shimadzu DTA/TGA-50, Japan with a heating rate of  $10^\circ\text{C min}^{-1}$  in nitrogen atmosphere. The flow rate of  $\text{N}_2$  was adjusted at  $20\text{ cm}^3\text{ min}^{-1}$ . For the FT-IR measurements, FT-IR Nexxus-Nicolite Model 640-MSA instrument was used. The dried samples were ground with KBr and then compressed as pellets under hydraulic pressure. The pellets obtained were oven dried again at  $70^\circ\text{C}$  for 1 h. RS, bleached Cellulose and Lignin were subjected to C/H/N elemental analysis.

#### Studies on the soil samples

Each soil was mixed with the concentrations 0.0%, 0.1% and 0.3% of the RS and its different fractions (RA, Cellulose, Silica and acid-insoluble Lignin). Each treatment reading was an average of three replicates, i.e. 11 amendment treatments  $\times$  2 soils = 22 treatments, with 3 reps each.

**Table 1**  
Some properties of the studied soil samples.

	Particle size distribution (g/kg)					OM (%)	$\text{CaCO}_3$ (%)	pH (1:2.5)	$\text{EC}_e^a$ (dS/m)	Soluble ions <sup>a</sup> (meq/L)						
	Coarse sand	Fine sand	Silt	Clay	Texture class					$\text{Ca}^{++}$	$\text{Mg}^{++}$	$\text{Na}^+$	$\text{K}^+$	$\text{HCO}_3^-$	$\text{Cl}^-$	$\text{SO}_4^-$
S1 soil	115	352.6	278.2	256.8	Sandy clay loam	2.46	23.04	8.23	4.28	1.81	0.9	1.4	0.19	1.48	0.83	1.97
S2 soil	747.7	190.1	48.8	10	Sand	0.25	0.89	7.99	2.24	1.26	0.44	0.36	0.17	0.56	0.46	1.22

<sup>a</sup> (1:5) soil extract.

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