INNSPUB
International Journal of Agronomy and Agricultural Research (IJAAR)
ISSN: 2223-7054 (Print) 2225-3610 (Online)
http://www.innspub.net
Vol. 3, No. 12, p. 21-35, 2013

RESEARCH PAPER

Studying the use of cellulose, silica and lignin extracted from rice straw as sandy soil conditioners

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Article published on December 08, 2013

Key words: Natural polymers, straw extracts, soil properties, nutrient uptake, soil conditioning.

Abstract

Rice straw is a renewable natural resource was recycled as an agricultural waste containing some natural bio-polymers. The study aims to evaluate the rice straw (RS) as well as straw ash (RA), Cellulose, Silica and Lignin extracted from the straw as environment friendly agricultural sandy soil conditioners. Some properties of these polymers are expected to affect some properties of soil as well as the macro-nutrient uptake by plant. The mentioned materials were extracted from RS then mixed with two soil samples different in their properties selected for the study and some of their properties were estimated. Soya bean and maize were germinated in different soil/conditioner mixtures and their nutritional content, NPK total content was estimated and the data were statistically analyzed. For the non-calcareous soil sample, the BD showed a relative decrease in the range 3.46% – 12.64% while the TP increased in the range 4.97 – 18.06% and the relative decrease in HC was in the range 5.63 and 91.82%. The accumulation of soluble salts, available and total NPK concentrations had been affected. The chemical structure of the studied biopolymers possessing functional groups (–NH, –OH, –COOH) and partial solubility of silica may offer chemical bonding and/or some other interaction with the different nutritional ions and adsorption sites affecting their solubility and availability within soil. The remediation effect is strongly dependent on the soil texture and salinity levels denoting to the chemical equilibria of the soil solution, accumulation of the soluble salts, nutrients in soil and the nutrient uptake by plants.

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Abbreviations:
RS, Rice straw; RA, rice straw ash; BD, bulk density; TP, total porosity; WHC, water holding capacity; FC, field capacity; HC, hydraulic conductivity; EC, electrical conductivity.

Introduction

Rice straw (RS) is the residue of rice production that was not utilized. The waste discharged can cause environmental problems and a loss of natural resources. If it can be utilized, it is no longer a waste but become a new resource. In agriculture, RS is often used for the compost production through the microbial activity which is then mixed with the rock phosphate and ammonium sulphate to be used as an organic fertilizer (Susmel *et al.*, 1991; Abdel-Mohdy *et al.,* 2009; Roca-Pérez *et al.,* 2009; Ali, 2011).

The RS with its complex structures is hard to be bio-degraded even by anaerobic microorganisms or degradation enzymes. It contains hemi-cellulose (~31.6%), cellulose (~38.3%) and lignin (~11.8%) in addition to high silica content (9-14%). 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 (Abdel-Mohdy *et al.*, 2009; Sang *et al.*, 2005; Yanfeng *et al.*, 2008; Chang *et al.*, 2010; Chang and Zhang, 2011). Lignin can bind heavy metal ions such as iron, copper and zinc. As a natural polymer, it is 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 (Shuzhen *et al.*, 2004; Xiao *et al.*, 2007; Yanfeng *et al.*, 2008).

Reclamation and land utilization of the desert areas, often sandy, are faced by several difficulties. To a large degree, the soil quality depends on the size, shape and arrangement of solids and voids. High sodium in Sodic soils or $CaCO_3$ content in some soils causes some difficulties such as reduced infiltration and poor drainage. Also, it causes the crop damage due to the standing water or inadequate aeration in the root zoon and in alga growth on the soil surface (Hussien *et al.*, 2012; Abdel-Mawgoud *et al.*, 2006; Abd El-Hamid, 2004; Abu-Hamdeh, 2004; El-Hady *et al.*, 1990; Abed *et al.*, 1981).

Sandy soils are often of light texture and residues; poor in nutrient, therefore applied fertilizers can easily be leached. Nitrogen (N) might be lost in soils by leaching or volatilization, while phosphorous (P) and potassium (K) might be fixed or leached (Molindo, 2009). Addition of humic substances to NPK fertilizer resulted in a lesser leaching N, K to deeper layer and higher available P (Selim *et al.*, 2010). Without input of fertilizers or other sources of plant nutrients, nutrient budgets are negative, resulting in soil fertility depletion (Saïdou *et al.*, 2003). On the other hand, regular application of commercial chemical fertilizers degrades soils physically and chemically and increase the input cost. They were used in such high amounts that they deteriorated soil health (Khan and Qasim, 2008).

The increased growth of a plant may be due to the optimum nutrient supply and better soil condition for growth of root and shoot (Yagoub *et al.*, 2012). N, P and K are among the most important nutrients for plant growth, and their diverse concentrations have a significant influence on the properties of soil-plant interface. Nutrient deficiency in soil can stimulate the release of exudates and alter plant growth patterns. Plant transpiration, photosynthesis, amino acid metabolism and biomass production, are also affected. Thus, the optimization of nutrient management is of great significance for reducing agro ecological risks associated with heavy metals pollution.

Salts are a common and needed part of the soil, and many salts (e.g., nitrates and potassium) are essential plant nutrients. But, they can become concentrated from natural processes and mismanagement. High soil salinity can also cause nutrient imbalances and reduce water infiltration if the level of one salt element - e.g. sodium - is high (Pace and Johnson, 2002). Salinity is usually not uniformly distributed in a field, but rather exhibit a heterogeneous distribution need for applying site-specific management to manage the movement of water in the soil. Adding good quality organic matter, sand with good quality compost can improve drainage. The NPK uptake was significantly affected by water levels since water supply is a major constraint to crop production (Abd El-Kader *et al.*, 2010).

Table 1. Some properties of the studied soil samples.

	Particle size distribution (g/kg)					OM (%)	$CaCO_3$ (%)	pH	EC_e*
	Coarse sand	Fine sand	Silt	Clay	Texture class			(1:2.5)	(dS m^{-1})
S1 soil	115	352.6	278.2	256.8	Sandy clay loam	2.46	23.04	8.23	0.86
S2 soil	747.7	190.1	48.8	10	Sand	0.25	0.89	7.99	0.45
	Soluble ions* (meq/L)								
	Ca^{++}	Mg^{++}	Na^{+}	K^{+}	HCO_3^{-}	Cl^{-}	SO_4^{-}		
S1 soil	1.81	0.9	1.4	0.19	1.48	0.83	1.97		
S2 soil	1.26	0.44	0.36	0.17	0.56	0.46	1.22		

***(1:5) soil extract**

Table 2. Hydro-physical properties of the studied soil samples and different treatments.

Treatment (wt/wt) on the air-dried basis)	BD		TP		S1*			S2*		
	S1	S2	S1	S2	WHC	FC	HC	WHC	FC	HC
Soil sample free of Conditioner	1.052 ^{a}	1.559 ^{ab}	60.3 ^{b}	41.177 ^{d}	b	c	ab	b	f	b
0.1% RS/soil mix.	1.053 ^{a}	1.505 ^{abc}	60.26 ^{b}	43.222 ^{c}	cd	c	b	ab	f	gh
0.3% RS/soil mix.	0.982 ^{a}	1.624 ^{a}	62.95 ^{a}	38.732 ^{e}	d	c	b	ab	e	h
0.1% RA/soil mix.	1.053 ^{a}	1.505 ^{abc}	60.26 ^{b}	43.222 ^{c}	bcd	c	ab	b	d	g
0.3% RA/soil mix.	1.055 ^{a}	1.362 ^{c}	60.18 ^{b}	48.614 ^{a}	bcd	c	b	b	bc	d
0.1% Cellulose/soil mix.	1.053 ^{a}	1.404 ^{bc}	60.26 ^{b}	47.007 ^{ab}	bcd	c	ab	b	d	f
0.3% Cellulose/soil mix.	1.055 ^{a}	1.407 ^{bc}	60.18 ^{b}	46.901 ^{b}	bc	a	b	a	cd	c
0.1% Silica/soil mix.	1.053 ^{a}	1.404 ^{bc}	60.26 ^{b}	47.007 ^{ab}	ab	ab	b	ab	bc	e
0.3% Silica/soil mix.	1.055 ^{a}	1.407 ^{bc}	60.18 ^{b}	46.901 ^{b}	a	b	b	b	ab	a
0.1% Lignin/soil mix.	1.053 ^{a}	1.404 ^{bc}	60.26 ^{b}	47.007 ^{ab}	bcd	c	a	b	bc	j
0.3% Lignin/soil mix.	1.055 ^{a}	1.407 ^{bc}	60.18 ^{b}	46.901 ^{b}	bc	c	b	ab	a	i

*Non-significant ranges at $P < 0.05$

RS as a renewable natural resource was recycled as an agricultural waste to obtain a number of natural bio-polymers that can be used as soil conditioners. Cellulose, Silica and Lignin extracted from the RS could be used as environment friendly sandy soil conditioners (Rashad, 2013). The swelling and/or adsorption properties of these polymers are expected to affect the hydro-physical properties of soil as well as the macro-nutrient uptake by plant.

Previous studies focused on the use of composted RS rather than its derivatives (Yagoub *et al.*, 2012; Ali, 2011; Roca-Pérez *et al.,* 2009).The present study aims to study the effect of use of the RS, RA, Cellulose, Silica and Lignin extracted from the straw on some of the soil hydro-physical properties, soluble ions, available and total NPK concentration in agricultural sandy soil. For this purpose, soya bean and maize were germinated in the soil samples mixed with different additives. Samples of soil mixtures were analyzed for their nutritional content and the results were discussed.

Materials and methods

Rice straw (RS) and it extracted conditioners

RS 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 °C for 10 h, and ground to pass through a 0.4 mm sieve. Carbonized straw ash (RA), Cellulose, Silica and acid-insoluble Lignin were extracted from RS according to the previously stated procedure[1].

Soils

Two agricultural 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 mm sieve and kept for the study. Some of their properties were estimated according to Page *et al.* (1982) 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.

Hydro-physical properties of the soil

Some hydro-physical properties of the soil free of amendments (control) as well as the soil/conditioner mixtures were carried out as follows:

BD

One hundred grams of the air-dry soil or soil/conditioner mixture sample was packed in the core (5 cm height × 5 cm diameter with two open ends; one end was sealed by a filter paper supported by a filter tissue) by gentle manual vibration. The core containing the sample was weighed then immersed in distilled water to the half of its height for overnight equilibrium. After that, the wet samples were removed from water, covered to prevent evaporation and left overnight to drain excess water then weighed again. The height of the soil column inside the core was measured then oven dried at 105 °C for 4 h (the core method (Black, 1982)). The BD values have been calculated according to the equation:

$$BD\,(g/cm^3) = \frac{\text{oven dried weight of soil column}(g)}{\text{volume of soil column}(\pi\, r^2\ X\ \text{soil height})\,(cm^3)}$$

(1)

Porosity was calculated from the measured BD, assuming a particle density of sandy soil of 2.65 g/cm³.

$$TP(\%) = \frac{\text{Particle density of sandy soil} - \text{Dry bulk density}}{\text{Particle density of sandy soil}} \times 100$$

(2)

HC

The sample packed core (15 cm height × 5 cm diameter) was saturated by moisture as described in the previous section. A small piece of blotting paper was placed on the top of the sample and water slowly poured into the upper cylinder until it is 2/3 to 3/4 full. The siphon is started to maintain a constant head of water on the soil column. After the water level on the top of the soil has become stabilized (after ~ 20-30 min), the percolates were collected in beakers at constant time intervals. The soil column remained saturated during the experiment (the constant head method (Klute and Direksen, 1986). The Ks of the soil to water was calculated according to the equation:

$$Ks\ (m/day) = \frac{QL}{HAT} \qquad (3)$$

Where Ks (cm/h which was plotted as m/day): the saturated hydraulic conductivity, Q (mL): the volume of the percolating water, L (cm): the height of the soil column inside the core, H (cm): the total head, A (cm²): the cross sectional area of the sample, T (h): the time of collecting percolates (0.5 and 0.25 h for S1 and S2 soil samples, respectively).

Seed germination

In a greenhouse pot experiment, 400 g of each soil was treated by the concentrations 0.0 (control), 0.1 and 0.3% of RS and its different fractions; RA, Cellulose, Silica and Lignin. Each treatment was replicated three times, i.e. 11 amendment treatments × 2 soils = 22 treatments, with 3 reps each. The experiment was completely randomized blocks.

Soya bean (4 seeds/pot) followed by maize (20 seeds/pot) were planted in both control and treated soil. The seedlings were subsequently thinned to 2-3 plants per pot after emergence. Plants were grown under greenhouse conditions (at 25 – 30 ^{o}C) during the day and (22 – 26 ^{o}C) during the night. Fertilization was carried out using a mineral fertilizer solution (NPK, 19% each + trace elements Zn, Mn and Fe) added to each pot. Plants were harvested after germination (28 days for soya bean – 14 day for maize) when reached a height of ≈ 15 - 20 cm and 20 - 25 cm for soya bean and maize, respectively. The aboveground parts were cut off, washed thoroughly with tab water then with distilled water. The plants were oven dried at 70 ^{o}C for 48 h, finely ground for the estimation of their total content of NPK. At the end of the experiment, soils were air dried ground and sieved by a 2-mm sieve then subjected to the analysis of their soluble cations and anions as well as their available NPK.

Estimation of soluble ions and nutrients

For soil

a. Soluble cations and anions

In a 1:5 soil:water suspension, the electrical conductivity (EC) value was recorded using an EC – meter (WTW series, InoLab – Cond. 720, Germany). Soluble HCO_3^-, Cl^-, Ca^{2+} and Mg^{2+} were determined using the standard titration method (Richards, 1954), while soluble SO_4^{2-} was obtained from the difference between the sum of soluble cations and anions. Soluble Na^+ and K^+ were detected by the flame photometer.

b. Available NPK

The soil available N was estimated by kjeldahl method. It was extracted by K_2SO_4 (1%) and determined by the distillation in a macro kjeldahl apparatus using MgO and Devarda alloy (Black, 1965). Available P was extracted by 0.5 N $NaHCO_3$, determined colorimetrically using stannous chloride mixture and measured spectrophotometrically at λ = 660 nm using JENWAY Spectrophotometer 6405 UV/Vis. Available K was extracted by 1 N ammonium acetate (NH_4OAc - pH 7.0) and determined by the flame photometer (Jackson, 1973).

For plant

a. Total NPK

After wet digestion of plant samples with conc. H_2SO_4 and $HClO_4$, total N was determined by distillation in a macro kjeldahl apparatus. Total P was estimated as mentioned previously, while K content was determined by the method mentioned by Dewis and Freitas (1970).

Statistical analysis

Data were statistically analyzed and are the mean values ± standard errors (n=3). The one-way analysis of variance (ANOVA) was carried out to determine the statistical significance of the treatment effects with the least significant difference procedure at a significance level of 0.05.

Results

RS, RA, Cellulose, Silica and Lignin used in this study can be classified in two types:

(a) Mainly organic additives including RS, Cellulose and Lignin, and

(b) Mainly inorganic additives including RA and Silica.

For both types, it can be said that the predominant functional group is the hydrophilic OH^-. Most of them are often blocked by the interaction between different constituents of RS while they are often freed upon separation of them. Such OH^- groups are capable to H-bonding with water molecules within the soil matrix. Additionally, some interaction through weak Van der Waal's forces, H-bonding and/or electrostatic attraction may occur between the particles of RS or its components and different soil particles in presence of the soil solution with its complicated composition. Attraction/repulsion phenomenon can be predicted to occur in soil solution between the hydrophilic OH^- and the different ions and nutrients soluble in solution. This is in turn will affect the chemical equilibria related to such osmotic effects.

Effect on the hydro-physical properties of soil

BD

The soil BD, void ratio and porosity are important measurements for the physical arrangement of solids and voids relative to each other. Table 2 shows the BD and TP% of both S1 and S2 soil samples before and after mixing with the studied conditioners. The BD of the soil S1 remained almost unchanged after mixing with the studied conditioners except for the higher concentration of the RS; it was decreased by 6.65% compared with the control sample. The relative decrease was calculated by dividing the value of the treatment by that of the control for each soil. For the S2 soil, the relative decrease in the BD was in the range 3.46% – 12.64% except for higher concentration of the RS for which the BD was increased by 4.17%.

Table 3. Electrical conductivity (EC) and concentrations of soluble ions of the studied soil samples.

(a) S1

Sample No.	**Sample Type**	**EC_e (dS/m)**	**Soluble ions (meq/L)**						
			Ca^{+2}	**Mg^{+2}**	**Na^{+}**	**K^{+}**	**HCO_3^{-}**	**Cl^{-}**	**SO_4^{-2}**
1	Control	1.83	3.83	1.97	1.79	1.58	0.62	1.04	7.51
2	RS 1	2.37	5.63	2.58	2.05	1.58	0.55	0.95	10.35
3	RS 2	1.74	3.64	2.26	1.66	1.13	0.74	1.02	6.94
4	RA 1	2.02	4.9	2.4	1.74	1.06	0.57	0.96	8.57
5	RA 2	1.83	4.15	2.47	1.33	1.18	0.68	0.88	7.57
6	Cellulose 1	2.18	4.28	3.33	1.75	1.54	0.33	0.69	9.88
7	Cellulose 2	1.81	3.71	1.89	2.06	1.42	0.59	0.7	7.78
8	Silica 1	1.93	3.66	2.39	2.21	1.38	0.67	1.02	7.94
9	Silica 2	1.38	3.07	1.19	1.32	1.33	2.07	0.79	4.05
10	Lignin 1	1.56	3.21	1.89	1.27	1.43	1.14	0.79	5.86
11	Lignin 2	1.78	3.11	2.76	1.72	1.3	0.5	0.6	7.8

(b) S2 : Sandy soil

Sample No.	**Sample Type**	**EC_e (dS/m)**	**Soluble ions (meq/L)**						
			Ca^{+2}	**Mg^{+2}**	**Na^{+}**	**K^{+}**	**HCO_3^{-}**	**Cl^{-}**	**SO_4^{-2}**
12	Control	0.48	0.49	1.22	0.26	0.45	1.38	0.35	0.68
13	RS 1	0.35	0.22	1.22	0.12	0.18	0.67	0.21	0.85
14	RS 2	0.55	0.77	1.47	0.25	0.22	0.67	0.26	1.8
15	RA 1	0.36	0.63	0.78	0.17	0.19	0.88	0.29	0.62
16	RA 2	0.54	0.96	1.09	0.3	0.39	0.66	0.76	1.3
17	Cellulose 1	0.43	0.41	1.28	0.23	0.21	0.63	0.42	1.08
18	Cellulose 2	0.49	0.26	1.69	0.24	0.27	1.05	0.61	0.8
19	Silica 1	0.37	0.4	0.91	0.26	0.27	0.91	0.64	0.29
20	Silica 2	0.41	0.71	0.94	0.18	0.21	0.5	0.57	0.97
21	Lignin 1	0.52	1.04	0.77	0.36	0.42	0.72	0.33	1.54
22	Lignin 2	0.44	0.77	1.02	0.19	0.23	0.54	0.44	1.24

Table 4. Available NPK of the studied soil samples,

(a) S1

Sample No.	Sample Type	Conc., g/Kg		
		N	P	K
1	Control	0.082^{e}	0.032^{h}	2.26^{a}
2	RS 1	0.076^{f}	0.09^{b}	2.17^{b}
3	RS 2	0.107^{a}	0.018^{i}	1.85^{e}
4	RA 1	0.082^{e}	0.046^{f}	1.85^{e}
5	RA 2	0.101^{b}	0.034^{h}	1.98^{d}
6	Cellulose 1	0.088^{d}	0.098^{a}	2.26^{a}
7	Cellulose 2	0.054^{g}	0.074^{c}	2.26^{a}
8	Silica 1	0.088^{d}	0.054^{e}	2.07^{c}
9	Silica 2	0.076^{f}	0.032^{h}	1.76^{f}
10	Lignin 1	0.107^{a}	0.062^{d}	1.48^{g}
11	Lignin 2	0.095^{c}	0.038^{g}	2.07^{c}

Different letters in rows indicate significant differences ***($P < 0. 05$)***.

(b) S2

Sample No.	Sample Type	Conc., g/Kg		
		N	P	K
12	Control	0.044^{e}	0.038^{gh}	0.312^{a}
13	RS 1	0.044^{e}	0.04^{fg}	0.264^{b}
14	RS 2	0.057^{c}	0.036^{h}	0.255^{c}
15	RA 1	0.032^{g}	0.05^{e}	0.264^{b}
16	RA 2	0.063^{b}	0.07^{a}	0.312^{a}
17	Cellulose 1	0.050^{d}	0.042^{f}	0.226^{e}
18	Cellulose 2	0.038^{f}	0.054^{d}	0.264^{b}
19	Silica 1	0.032^{g}	0.06^{c}	0.255^{c}
20	Silica 2	0.047^{de}	0.066^{b}	0.264^{b}
21	Lignin 1	0.069^{a}	0.062^{c}	0.312^{a}
22	Lignin 2	0.038^{f}	0.068^{ab}	0.248^{d}

Different letters in rows indicate significant differences ($P < 0.05$).

Since the weight of the soil/conditioner mixture cannot be decreased due to the absorbed water, its volume is expected to increase and hence the BD decreases. This may occur when the soil particles rearrange, re-aggregate and make different texture under the effect of the bound and trapped water molecules. This effect was more pronounced for the S2 in the case of RA, Cellulose, Silica and Lignin with the nearly pure chemical composition of free –OH. Highly fine particles as well as the higher concentration of soluble ions of the S1 soil solution may restrict both the re-aggregation of soil particles and their interaction with the absorbed water and/or conditioners. Hence, its BD had not been affected and higher concentration of treatments may be required (Hussien *et al.*, 2012).

Table 5. Total NPK of Soya bean and maize germinated in the S1 soil samples.

(a) Soya bean

Sample No.	Sample Type	Conc., g/Kg		
		N	P	K
1	Control	36.23^{g}	2.38^{b}	35.34^{e}
2	RS 1	50.4^{c}	1.5^{f}	34.16^{f}
3	RS 2	44.1^{d}	2.25^{c}	32.98^{g}
4	RA 1	40.95^{f}	0.25^{i}	32.98^{g}
5	RA 2	51.98^{b}	1.75^{d}	35.34^{e}
6	Cellulose 1	36.23^{g}	0.75^{h}	40.27^{b}
7	Cellulose 2	40.95^{f}	1.38^{g}	39^{c}
8	Silica 1	40.95^{f}	0.75^{h}	31.05^{h}
9	Silica 2	42.53^{e}	1.38^{g}	31.05^{h}
10	Lignin 1	29.65^{h}	1.62^{e}	36.53^{d}
11	Lignin 2	78.75^{a}	4.5^{a}	46.31^{a}

Different letters in rows indicate significant differences *($P < 0.05$)*.

(b) Maize

Sample No.	Sample Type	Conc., g/Kg		
		N	P	K
1	Control	31.5^{j}	5^{b}	64.6^{g}
2	RS 1	45.68^{c}	4.63^{d}	82.5^{b}
3	RS 2	33.08^{i}	4.38^{e}	64.6^{e}
4	RA 1	36.23^{h}	3.25^{g}	56.8^{f}
5	RA 2	44.1^{d}	4.75^{c}	64.6^{e}
6	Cellulose 1	42.53^{e}	4.38^{e}	84.5^{a}
7	Cellulose 2	47.25^{b}	4.75^{c}	79.7^{c}
8	Silica 1	40.95^{f}	3.38^{f}	56.8^{f}
9	Silica 2	42.53^{e}	2.69^{h}	56.8^{f}
10	Lignin 1	48.83^{a}	5.56^{a}	67.4^{d}
11	Lignin 2	39.38^{g}	4.44^{e}	79.7^{c}

Different letters in rows indicate significant differences *($P < 0.05$)*.

TP

The TP% values of the S1 treatments were compatible with their BD results. This is because the finer textured S1 soil particles might be easily compressed, collapse voids and reorient and hence counteract the hydrophilic effect of RS or its extracted components.

For the S2 soil sample, the TP% was slightly increased for different treatments. The relative increase was calculated by dividing the value of the treatment by that of the control. It was in the range 4.97 – 18.06%. It might be due to the increase in the pore space between coarse sand particles re-oriented by the effect of hydrophilic nature of conditioners on the soil particles (Hussien *et al.*, 2012).

WHC and FC

Fig. 1(a,b) shows only slight change in the WHC and FC of S1 treated by Cellulose and Silica compared to its control sample. For S2, although small difference was observed in the WHC among different treatments, a wider difference had occurred in the corresponding FC. This means that water absorbed by soil treated by additives had been kept and stored to a high degree. This may strongly support the concept of the H-bonded water by the hydrophilic additives mentioned (Bhardwaj and Mclaughlin, 2007; Andry *et al.*, 2009; Bhat *et al.*, 2009; Hussien *et al.*, 2012).

Table 6. Total NPK of Soya bean and maize germinated in the S2 soil samples

(a) Soya bean

Sample No.	Sample Type	Conc., g/Kg		
		N	P	K
12	Control	45.68 ^{b}	0.76 ^{i}	25.92 ^{i}
13	RS 1	31.5 ^{g}	0.9 ^{h}	29.45 ^{h}
14	RS 2	31.5 ^{g}	1.75 ^{c}	32.98 ^{e}
15	RA 1	35.5 ^{f}	1.1 ^{f}	32.53 ^{f}
16	RA 2	45.68 ^{b}	1 ^{g}	31.81 ^{g}
17	Cellulose 1	27.8 ^{h}	1.62 ^{d}	34.65 ^{d}
18	Cellulose 2	48.83 ^{a}	1.38 ^{e}	41.44 ^{a}
19	Silica 1	39.38 ^{d}	3.38 ^{a}	35.34 ^{c}
20	Silica 2	37.8 ^{e}	1.13 ^{f}	24.75 ^{j}
21	Lignin 1	23.63 ^{i}	2.63 ^{b}	31.81 ^{g}
22	Lignin 2	40.95 ^{c}	1.63 ^{d}	39 ^{b}

Different letters in rows indicate significant differences ($P < 0.05$).

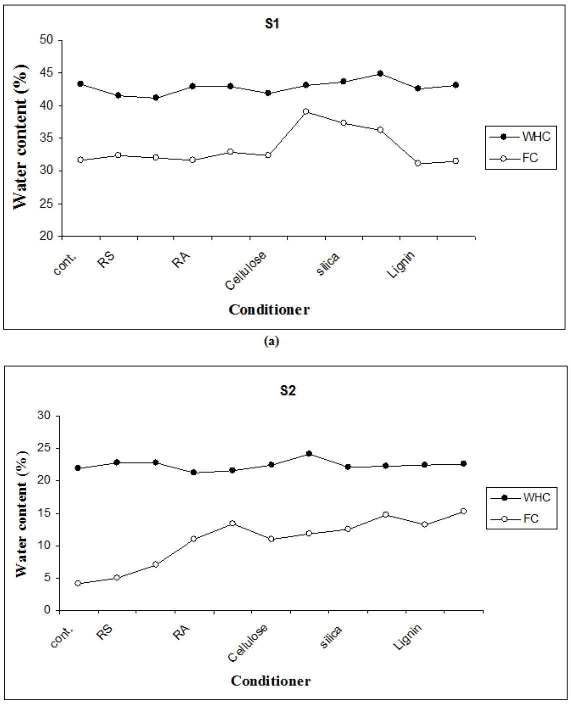
(b) Maize

Sample No.	Sample Type	Conc., g/Kg		
		N	P	K
12	Control	47.25^{a}	1.25 ^{i}	48.8 ^{g}
13	RS 1	33.25 ^{f}	1.39 ^{h}	39.0 ^{h}
14	RS 2	33.25 ^{f}	1.53 ^{g}	39.3 ^{h}
15	RA 1	31.5 ^{g}	2.38 ^{e}	54.3 ^{e}
16	RA 2	45.82 ^{b}	2.27 ^{f}	51.4 ^{f}
17	Cellulose 1	23.63 ^{i}	2.38 ^{e}	54.3 ^{e}
18	Cellulose 2	29.93 ^{h}	3.13 ^{a}	62.01 ^{a}
19	Silica 1	34.65 ^{e}	3 ^{b}	55.6 ^{d}
20	Silica 2	31.5 ^{g}	2.88 ^{c}	56.8 ^{c}
21	Lignin 1	42.53 ^{c}	2.75 ^{d}	56.8 ^{c}
22	Lignin 2	36.23 ^{d}	2.75 ^{d}	59.5 ^{b}

Different letters in rows indicate significant differences ($P < 0.05$).

HC

The HC expressed as Ks of a soil is a measure of its ability to transmit water. Fig. 2 shows the Ks of the S1 soil treatments. The Ks values had decreased and the relative decrease was in the range 32.9 – 93.03% compared to the control soil sample. This may be due to the decrease in the pore space between the soil particles and aggregates. The presence of additives particles might accommodate such space at the expense of some soil capillaries available for the water movement. Consequently, the volume of the water-conducting pores decreased. The permeability of the compacted matrix and thus the Ks had been decreased by the increased concentration of the additives.



(a)

(b)

Fig. 1 (a and b). Water holding capacity (WHC) and Field Capacity (FC) of the studied soil samples and different treatments.

For the S2 soil, although the TP% has increased, the Ks values were less than those of the control sample except for the high concentration of Silica. The relative decrease ranged between 5.63 and 91.82%. The quickly drainable pores (QDP) perhaps have been reduced and the Ks would be mainly controlled by the more fine pores as the slowly drainable pores (SDP) and the fine capillary pores (FCP). Fast Ks suggests that the volume of the water-conducting pores within the column of the soil was increased. The pressure applied by the hydraulic head as well as the surrounding soil particles might be expected to cause leaching and drainage of the swollen Silica particles. The pore space occupied by the particles would be decreased; the capillary pore space available for the water flow increased and thus the Ks increases (Bhardwaj and Mclaughlin, 2007; Andry *et al.*, 2009; Bhat *et al.*, 2009; Hussien *et al.*, 2012).

Statistical analysis

Table 2 shows the non-significant ranges for the studied soil properties affected by different additives. Compared to the control soil sample, non-significant variation was the predominant behaviour for S1 while some significant variation ranges have been observed for S2. Major treatments of Cellulose, Silica and Lignin had increased the TP and FC while decreased the BD and HC of S2 significantly.

Effect on the soluble cations and anions

Tables 3(a,b) indicate that the electrical conductivity (EC) of the soil extract was affected by the presence of the different additives within the soil matrix. Soluble ions might be trapped and accumulated within the soil with different degrees depending on the soil texture and the concentration of the added material.

Relative increase/decrease was calculated by dividing the value of the treatment by that of the control for each soil. For S1, EC decreased compared with the control in the range (2.73% - 24.6%) for the higher concentration of RS, Silica and both treatments of Lignin. For S2, EC increased (2.1% - 14.58%) for the higher concentration of RS, RA, Cellulose and the lower concentration of Lignin. Trend was reflected by the behaviour of the divalent cations Ca^{+2} and Mg^{+2}. Some EC values have exceeded that of the control and some was lower. A mono-valent cation (attracting a mono-valent anion in solution) competes for a negatively charged site more than the divalent one. So, mono-valent ions are expected to be less labile due to their presence nearby the hydrophilic sites bearing OH^- forming electric double layer and leaving divalent ions in the bulk of soil solution or at least; more labile.

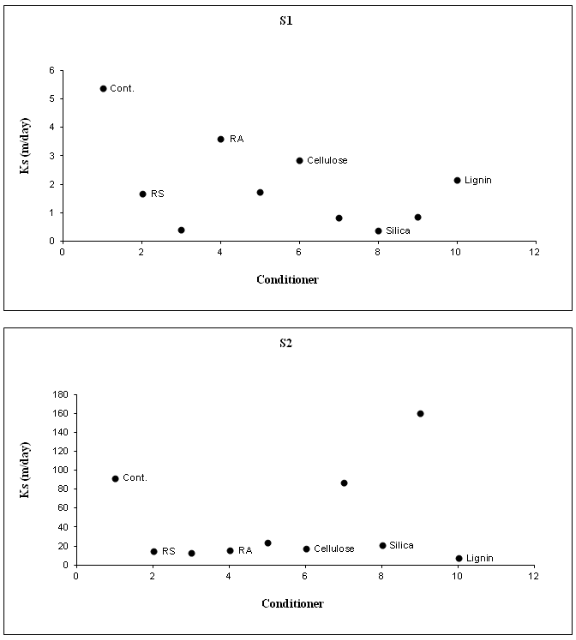


Fig. 2. Hydraulic conductivity of the studied soil samples and different treatments.

Effect on the available NPK

According to Tables 4(a,b), the effect of different additives on the soil available NPK can be discussed as follows:

Nitrogen (N)

No single regular trend could be observed for N among treatments. For both S1 and S2, available N increased for some treatments (RS and RA) as their concentration increases but it decreases for some other (Cellulose and Lignin) as their concentration increase compared with the control.

Phosphorous (P)

Available P had increased for different treatments compared to the control. The range of relative increase for S1 was (6.25 - 206.25%) except for RS and Silica at their higher concentration treatment while for S2 it was (5.26 - 84.21%) except for the higher concentration of RS.

Potassium (K)

Available K was decreased for different treatments compared to the control. The range of relative decrease was (3.98 - 34.51%) except for Cellulose treatments for S1 while it was (15.38 - 27.56%) except for the higher concentration of RA and the lower one of Lignin.

Effect on the Total NPK

According to Tables 5(a,b) and 6(a,b), the effect of different additives on the plant total NPK can be discussed as follows:

Nitrogen

A general trend with two opposite behaviours for the total N could be observed. For both soya bean and maize, the total N had increased for treatments compared with the control for S1 but decreased compared with the control for S2. (Relative increase: soya bean 13.03 - 117.36%, maize 5.02 - 55.02%; Relative decrease: soya bean 10.35 - 48.27%, maize 3.03 - 49.99% for S1 and S2, respectively).

Phosphorous

Also, a general trend with two opposite behaviours for total P can be observed. For both soya bean and maize, the total P has decreased for treatments compared with the control for S1 but increased compared with the control for S2. (Relative decrease: soya bean 5.46 - 89.5%, maize 5 - 46.2%; Relative increase: soya bean 18.42 – 344.08%, maize 11.2 – 150.4% for S1 and S2, respectively).

Potassium

Total K behaved a different manner for plants germinated in S1 treated by different additives. Total K has increased for some treatments (the highly organic additives; Cellulose and Lignin) but decreased or unchanged for other (less organic RS and inorganic RA and Silica) compared with the control for both soya bean and maize. For S2, the total K has generally increased for treatments except for the higher concentration of silica for soya bean and RS for maize. (Relative increase: soya bean 13.62 - 59.88%, maize 5.33 - 27.08%).

Discussion

The electrical conductivity (EC), accumulation of soluble salts, available and total NPK concentrations had been affected by the addition of RS or its extracted conditioners to the soil samples. The effect on the fine calcareous sandy soil (S1) was less pronounced than that on the coarse non-calcareous soil (S2). For the S1, higher concentration of some additives may be required. This is often related to the effect on some of the hydro-physical properties of the soil like BD, WHC, FC and HC. Lower concentration of the highly organic and the chemically pure additives; Cellulose, Silica, Lignin and finally RA are sometimes more effective than the raw RS.

Among treatments, Silica treatments showed lower total PK values for plants germinated in S1 but higher values for those germinated in S2. This may suggest a higher affinity towards phosphorous and potassium exhibited by the smaller size and the highly hydrophilic Silica particles compared with the bulky particles of other additives. Silica could interact physically or chemically with ionic nutrients through silanol groups Si – OH and form nutritive species that are available for plant uptake (Rizwan *et al.*, 2012; Gu *et al.*, 2011; Gunes *et al.*, 2007; Ge´rard *et al.*, 2008; Shenol, 1999). It could be said that the presence of Si nearby the root zone may enhance the PK uptake by plant. This availability might be restricted through the S1 soil matrix due to the more compacted fine textured particles which resist the mobility of nutritive species in the soil solutions.

The total NPK values of Cellulose and Lignin treatments sometimes had exceeded those of other treatments (e.g. Table 5b). As being organic amendments, their need to complementary fertilizers may be case studies.

Total N for plants germinated in S1 was mainly higher than those germinated in S2. Nitrogen might be lost from S2 either by evaporation or leaching from the root zone. Another suggestion is that N has been fixed by the functional groups (– NH, – OH, – COOH …etc.) of the different additives competing with P and K and making them more available for plant (Yanai, 2007).

Conclusion

Addition of RS, RA, Cellulose, Silica and Lignin to an agricultural sandy soil had affected its electrical conductivity (EC), accumulation of soluble salts, available NPK concentrations and total plants' NPK. This is may be strongly related to the chemical structure of such biopolymers and their functional groups (– NH, – OH, – COOH …etc.) content. Chemical bonding and/or some other interaction between such groups and the different nutritional ions and adsorption sites should affect their solubility and availability within soil. The possible partial solubility of silica is an additional affecting factor. The effect on the fine calcareous sandy soil was less pronounced than that on the coarse non-calcareous soil. This is often related to the effect on some hydro-physical properties of soil such as BD, WHC, FC and HC. Lower concentration of the highly organic chemically pure materials which are Cellulose, Silica, Lignin and finally RA is sometimes more effective than RS. Silica may be distinguished by its ability to be a source of silicon (Si) as a nutrient. Its effect is more pronounced in the coarse non-calcareous sandy soil than in the fine textured calcareous sandy soil. The need of Cellulose and Lignin to complementary fertilizers may be case studies.

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