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Evaluating the grafting approaches for utilizing the rice straw as environmental friendly and potential low cost hydrogels

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Abstract

The present work deals with producing water absorbent hydrogels from rice straw (RS) without any pretreatment. The utilization of RS (an undesirable bio waste) for production of the required hydrogels will add highly to the economic value, contribution reducing the environmental impact of waste disposal and most importantly provide a potentially inexpensive alternative biopolymer to the existing commercial hydrogels from petrochemical origins. The required hydrogels were prepared on a Lab- and Pilot scale via different graft copolymerization approaches with acrylonitrile, by using a technique which reduces the environmental impact, resulting from loading of waste-water by non-reacted monomer, to a minimum. The prepared hydrogels were characterized by using chemical analysis, IR- spectra and thermo gravimetric analysis TGA analysis. As well as, the role of grafting approach and pH-value on affinity of the hydrogels produced to absorb water (distilled and Nile water) was evaluated. The results obtained show that, grafting of precyanoethylated RS, using persulfate-persulfite initiation system, followed by alkali hydrolysis provide hydrogel with relatively higher absorption capacity towards both distilled and Nile water than using Ferrous sulfate-H_2O_2 initiation system. The candidate hydrogels have no toxic (inhibitory) effect against the most efficient micro-organisms in plants media (rhizosphere).

Key words: Hydrogels, Agricultural waste management, Rice straw, Eco-grafting approach, Water absorbent biopolymer, Biopolymer application

Introduction

Sandy soils are wide spread in Egypt and other countries of the Middle East. They cover vast areas that can help in solving the shortage in food production. Incorporating highly water-absorbent polymers (hydrogels), in sandy soil is one technique used as soil conditioners.

Highly water-absorbent materials were first discovered by a group at the North Regional Research Laboratories in the course of an application study of graft copolymers of starch (Burr et al., 1976; Fanta et al., 1984). Presently, there is more than one method for the preparation of hydrogels such as: (a) Hydrogels from industrial polymers [e.g., the preparation of β-acryloxypropionic acid from the chemical initiating the monomer of ethylene glycoldimethacylate (Ansel, 1995). (b) Hydrogels from conventional chemical modification of rice hulls by concentrated nitric acid or phosphorylation of cellulosic material (Saito et al., 1991; Buchholz and Peppas, 1994; Saito et al., 1995), and (c) Hydrogels from graft copolymerization of starch, cellulose, by-products hemicelluloses and lignin, as well as cellulose and chitosan derivatives with vinyl monomers containing a carboxyl, sulfonic, or nitrile group, in the presence of cross-linking agents. In the case of using acrylonitrile as a vinyl monomer, the alkali hydrolysis must be carried out on the prepared grafted samples (Kennedy et al., 1993; Athawale and Lele, 2000; Li and Pan 2010; Singh et al., 2012). Copolymerization of acrylamidomethyl propane sulfonic acid and acrylonitrile onto starch resulted in hydrogel materials without needing an alkali hydrolysis stage.

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In 1990, in the framework of cooperation between the International Trade Ministry and the Industrial Ministry of Japan, the Japanese Aids Programe used highly water-absorbent product as a soil conditioner for sandy soil in Egypt. However, this experiment had failed because of unfixation of hydrogels toward light.

In the previous investigations (Fanta and Doane, 1990; El-Saied et al., 2000; Kume et al., 2002), hydroxyethyl cellulose (HEC) and other polysaccharides (i.e., konja mannan, alginic acid, agar, pectin, starch and chitin) were selected as the trunk polymers, these polysaccharides were prepared as graft copolymers with partially hydrolyzed polyacrylamide (PAM) or polymethyl acrylate (PMA), poly-(2-dimethylamino) ethyl-methacrylate (PDM) or polyacrylic acid sodium and potassium salts (PAANa), to give highly water absorbent- materials. The wastewater from grafting process loads of non-reacted monomer (harmful compound). Synthetic polymer (e.g., polyacrylamide) in gel form are considered as one of the most widely used materials as soil conditioning for sandy soils, when mixed with such soils (Karlsson, 2000).

Although the extent of application of the synthetic soil conditioner polymers is very wide, especially in desert area, their use in practice is not spread as expected due to high cost. Despite the agricultural wastes represent an inexpensive source of lignocellulosic cellulose products, e.g., artificial wood and paper, most of it caused pollution due to there are good media for growing the microorganisms, or emission of toxic gasses during disposal by burning. The utilization of lignocellulosic wastes, as cellulose source, for economical preparation of hydrogel was studied by numerous authors (Buchholz and Peppas, 1994; Saito et al., 1995). This hydrogel was prepared from chemical treatment of rice hulls by concentrated nitric acid or phosphorylation of cellulosic material.

In Egypt and other similar countries, which have huge amount of agricultural wastes (lignocelluloses), e.g., rice straw, sugar-cane bagasse, cotton stalks etc, normally they use partially in pulp and paper industries, however they are still large amounts, especially RS without any utilization and cause environmental problems. According to the periodical report of Ministry of Agriculture in Egypt for the year 2009, the accumulated quantities of rice straw was about 6 million ton/year.

In our previous work (El-Saied et al., 2000, 2004, 2007), hydrogel was prepared from local endogenous lignocelluloses in pulp form, e.g., sugar-cane bagasse, rice straw and cotton stalks. These hydrogels were prepared via graft copolymerization reactions with some vinyl monomers, using a new technique which reduces environmental impact, resulting from unreacted monomer, to a minimum. The pore size distribution and its relation with moisture retention capacity (as a preliminary examination) of sandy soil loaded with hydrogel-based lignocellulosic materials recommended the utilization of such material as soil conditioner. So it is aimed to evaluate in detail, the utilization of these foregoing hydrogels as soil conditioner in sandy soil, comparing to other conventional soil conditioners (organic fertilizer and bentonite). Despite the success of this technology to overcome the agronomic obstacle of sandy soil, their use in practice has not been recommended due to it needs pretreatment to reduce the noncellulosic constituents, which add cost during production as well as environmental impact from disposal of treatment liquors.

The present work deals with producing hydrogels from raw rice straw (RS) without any pretreatment. The role of grafting approach and type of acid used to neutralize the gel, on affinity of the hydrogel produced to absorb water (distilled and Nile water) was evaluated. In forthcoming work we will be concerned on evaluating these RS-based hydrogels as preserving agents for fertilizers in sandy soil, and as adsorbents for utilization of industrial waste water in irrigation purpose. The safe use of the investigated hydrogels as soil conditioners was also evaluated from examining their toxicity behavior against the most efficient micro-organisms in plants media (*rizosphere*).

Experimental

Grafting of rice straw in lab scale

In this work grafting of RS with acrylonitrile monomer, using radical intermediate were selected. The following initiation systems were applied;

Grafting via Hydroxyl Radical Initiation

Based on our previous work (El-Saied et al., 2007), ferrous ammonium sulfate- hydrogen peroxide-thiourea dioxide system, was used, as such system is regarded as the most suitable initiator onto carbohydrate. The graft copolymerization was carried out through a two-stage process. In the first stage the grinned RS (2-3 cm), without any purification, was impregnated with 0.1% ferrous ammonium sulfate, in a liquor ratio of 20 (wt/vol), for 15 min. at room temperature(~ 30°C). Then it was filtered under suction and pressed to remove the excess ferrous ammonium sulfate. For the second stage, the desired amount of H_2O_2 (0.12 of 30% soln. /based on RS), and thiourea dioxiode (equivalent the amount of H_2O_2, wt/wt) were added to the treated lignocellulose (RS). The mixture is adjusted to pH 6.5 followed by adding different ratios of monomer acrylonitrile (AN) with a few drops of emulsified soap and completing the solution to a liquor ratio of 20. The reaction was left to desired time (3 h) and temperature (75°C). The grafted samples were filtered, washed several time with water until neutralized and left in a vacuum oven at 65°C to dry. The effects of temperature (50°C instead of 75°C) of grafting and concentration of H_2O_2 (0.02-0.16), were also studied.

Grafting via Persulfate Initiation

The grinned raw (RS) were treated with the required amount of AN and emulsifier, followed by addition of the persulfate salt (0.6-3%) with good mixing, and finally added the calculated amount of bisulfate salt (0.3-1.5%) with continuing the mixing for the required time (3 h) at 45°C. The prepared copolymers are filtered, washed several times with water until neutralized and dried in a vacuum oven at 65°C.

The efficiency of grafting of vinyl monomer to lignocellulose using foregoing initiating systems are determined by determination of polymer load and homopolymers, from nitrogen content, using Kjehldal method, before and after soxhelet extraction for 48 h by dimethylformamide.

Preparing Hydrogels on a Pilot Scale

In this study the preparation of hydrogels were carried out through the following two steps:

Grafting Copolymerization for synthesis polyacrylonitrile-grafted-rice straw; PAN-g-RS (first step)

The promising grafting efficiencies of previous mentioned grafting processes were used to produce hydrolyzed grafted copolymer (HPAN-g-RS) on a pilot-scale. In both processes air dry milled (RS) was used (~1.5Kg) and mixed with AN (~3Kg) in presence of different initiators. About 4.5 Kg of the produced hydrolyzed copolymers are obtained. AN was grafted by using hydroxyl radicals (Fe2+ / H_2O_2 and persulfate initiator) according to the selected conditions which were provide higher monomer conversion;

- 0.16H_2O_2 (30%), 2AN, both based on oven dryweight of RS and liquor ratio 20, at temp. 50°C for .3 h), and
- 2.4% persulfate, 1.2 % bisulfite, 2 AN/RS, and liquor ratio 20, at temp. 50°C for .3 h)

The grafting step was carried out in stationary-tank mixture of capacity 60 l, with a driving motor of 1.6 hp, connected with a gearbox to stir at 23 rpm/min.

For the trial to enhance the persulfate-persulfite initiation system to produce high grafted RS, cyanoethylation of RS was carried out as pre-activation step. In this process RS was treated by 5% NaOH (based on RS), and 10% from the total amount of AN used in grafting, for 1 h, at room temperature (~35 °C), followed by adjusting the pH to 6-7. The grafting process was carried out under the same conditions of persulfate-persulfite initiation system, but by using the remained per cent of AN (90%).

Alkali Hydrolysis of Polymerized Rice Straw (second step)

The above prepared PAN-g- RS were subjected to alkali hydrolysis by KOH, to improve its absorbent properties. The experimental conditions of hydrolysis are 0.6 mole KOH per mol of AN, which is used in grafting, a 30 liquor ratio, and a temperature between 90°C and 100°C for 2h. The excess alkali was neutralized with dilute mineral and organic acids.

Characterization of PAN-g- RS and hydrogels

PAN-g-RS and HPAN-g-RS products were characterized by the following techniques:

Fourier transform infrared (FTIR)-spectra measurement

IR-spectra (4000-400 cm^{-1}) were recorded on Nexus 670 FTIR spectrophotometer (Iclet Co., USA), using KBr disc. The technique of O'Connor et al (O'Connor et al., 1958) was used to calculate the crystallinity index (Cr.I). The mean strength of hydrogen bonds (MHBS) was calculated according to Levdik et al. (1967).

Thermal analysis

Thermal gravimetric (TGA) and derivative of thermaogravimetric (DTG) analyses of the examined samples were done using a PERKIN ELIMER Thermogravimetric Analyzer (TGA 7). The analyses were performed with a heating rate of 10°C/min and a flow rate of 50 ml /minute, under non-isothermal conditions and in the presence of nitrogen.

TG-curve analysis

Kinetic studies, based on the weight loss data, were obtained by TG curve analysis. The activation energy has been evaluated by applying Coat and Redfern (1964), method of analysis. For pseudo homogeneous kinetics, the irreversible rate of conversion of the weight fraction of reactant was expressed by the following equation:

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \qquad (1)$$

Where, α is the fraction of material decomposed at time t, k is the specific rate constant and n is the order of reaction. The temperature dependence of k is expressed by the Arrhenius equation:

$$k = A\,e^{-Ea/RT} \qquad (2)$$

Where A is the frequency factor (s^{-1}) and T is the absolute temperature.

For linear heating rate, a, ($deg.min.^{-1}$):

$$a = \frac{dT}{dt} \qquad (3)$$

For calculating the activation energy, Ea, of thermal decomposition when n = 1, equation 4 was used.

$$\log\left[-\log\frac{1-\alpha}{T^2}\right] = \log\frac{AR}{aE_a}\left[1-\frac{2RT}{E_a}\right] - \frac{E_a}{2.3RT} \qquad (4)$$

When n ≠ 1, equation 5 was used;

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \log\frac{AR}{aE_a}\left[1-\frac{2RT}{E_a}\right] - \frac{E_a}{2.3RT} \qquad (5)$$

Plotting the left-hand-side value of the equation { i.e., $\log[1-(1-\alpha)^{1-n}/T^2(1-n)]$} against 1 / T using various values of "n" should give a straight line with the most appropriate value of "n" (Basta, 1999). The Least square method was applied for the equation, using values of "n" ranging from 0.0 to 3.0 in increments of 0.5. The correlation coefficient (r) and the standard error (SE) were calculated for each value of "n". The "n" value, which corresponds to the maximum r and minimum SE, is the order of the degradation process. The activation energies and frequency factors were calculated from the slope and intercept, respectively, of the Coat-Redfern equation with the most appropriate value of "n".

Water absorption capacity

In this study certain weight of the hydrogel produced was set in sufficient amount of distilled water or Nile water for 24 hours. Excess water over the swollen samples was weighed (W_1), then dry in oven at 105°C and weighed again (W_2).

$$\text{Water absorption} = \frac{W_2 - W_1}{W_1} \times 100$$

Toxicity (inhibitory) test against the most efficient micro-organisms in plants media (rhizosphere)

This test was carried out according to the following steps (Abdel-Hameed et al., 2008):

- In 100 ml flasks, each medium was inoculated with the proper microorganism and incubated at 28-30°C for 7 days for total microbial count and 15 days for the other microorganisms.
- After incubation period, 5 ml from each inoculated medium were diluted to 400 ml using the same medium (but not inoculated with the micro -organism) and was poured into sterile Petri dishes (10 ml/ each dish).
- To examine the degree of toxicity (the anti - microbial activity) for the prepared hydrogels on examined microbes, four small blocks of the solidified medium were cut out from the plates by means of sterile 0.5 cm cork borer and removed with a sterile needle. In the well-formed, a piece of each hydrogel (100 mg each) was placed. The dishes were incubated at the degree of 28-30°C for the proper time (15 days). The same experiment was triplicated. The anti-microbial activities were expressed as the width of zones of inhibition in millimeters. The affected area in each dish was counted and the mean of replicates was recorded (Abdel-Hameed et al., 2008).

Results and Discussion

Table 1 indicates the average values of the chemical compositions obtained from analyzing different types of available rice straw (RS). Chemical analyses were determined by standard methods (Markblatt IV/29, Jayme and Sarten, 1940; The Institute of Paper Chemistry, 1951).

Table 1. Chemical composition of rice straw.

Analysis	Mean value ±SD
Extractive(MeOH/Benzene)	3.05±0.141
Ash	16.60±0.622
Lignin	12.01±0.157
Pentosans	21.70± 0.481
Hollocellulose (free ash)	55.01±1.532

Effect of grafting approach (in Lab. Scale)

The polymer load and the monomer conversion percentages were recorded in Tables 2-4. For grafting via hydroxyl radical initiation, using Fe^{+2}-H_2O_2 system, Table 2 shows that, increasing the AN/RS ratio from 0.5 to 2 accompanied by increasing the polymer loading from 7.5% to ~61%, and there is no increase in the percent of grafting with further increase this ratio than 2. As can be noticed that, lowering the temperature of graft copolymerization from 75°C to 50°C has a profound effect (increased) the polymer loading of RS; whereas the polymer loading increased from ~ 61% to 85.504%.

On studying the effect of H_2O_2 concentration on polymer load percentage, under the foregoing optimum temperature and AN/RS ratio, Table 3 shows that at relatively high H_2O_2 concentration 0.16% based on RS optimum polymer load (92.39%) and monomer conversion (46.193%) percentages are obtained. The explanation of this observation depends on the following mechanism (Bains, 1972; Kolthoff and Barney, 1951);

- When Fe^{2+} ions are mixed with H_2O_2, $HO^{\cdot}$ radicals are generated.

$$H_2O_2 + Fe^{2+} \longrightarrow HO^{-} + HO^{\cdot} + Fe^{3+},$$

$$HO^{\cdot} + Fe^{3+} \longrightarrow HO^{-} + Fe^{2+}$$

- The $HO^{\cdot}$ radicals further decompose H_2O_2

$$HO^{\cdot} + H_2O_2 \longrightarrow H_2O + HO^{\cdot}_2,$$

$$HO^{\cdot}_2 + H_2O_2 \longrightarrow HO^{\cdot} + H_2O + O_2$$

The formed hydroxyl radical initiate both the grafting reaction between AN and RS with the formation of PAN-g-RS, or polymerization of AN with the formation of PAN (homopolymer). The decomposition of H_2O_2 by the hydroxyl radicals takes place only if H_2O present in large excess over Fe^{+2} ions (Kolthoff and Barney, 1951).

For the second grafting initiation system (per sulfate-bisulfite) in comparison with ferrous-hydrogen peroxide system, Tables 2-4 show that, the maximum polymer loading and AN conversion percentages were obtained on using 2.4% persulfate. This value is higher (149.385) than that obtained by Fe^{2+}-H_2O_2 initiation system (92.386). The change in persulfate is more significant on these grafting parameters than the case of Fe^{+2}-H_2O_2 system.

Table 2. Effect of Acrylonitrile to Rice straw ratio on grafting efficiency.

Exp.no.	AN/RS	Nitrogen %±SD	Polymer loading, % ± SD	Monomer conversion, % ±SD
1	0.5 : 1	1.83 ± 0.198	7.59 ±0.764	15.19± 2.160
2	1 : 1	2.88 ± 0.265	12.50 ± 1.022	12.5 ±1.445
3	2 : 1	9.81 ±0.495	60.87 ± 1.91	30.435±2.699
4	3 : 1	7.70 ±0.485	42.24 ± 1.870	14.08 ±2.646
5*	2: 1	11.95±0.306	85.504 ± 1.180	42.752 ±1.689

N.B: Liquor ratio is 20 : 1, H2O2 : 0.12, for 3h at 750C.

* the same Expt. conditions but at temp. 50oC

Table 3. Effect of H_2O_2 concentration on grafting efficiency.

Expt.no.	H_2O_2 (30%) / RS	Nitrogen, % ±SD	Polymer loading,% ±SD	Monomer conversion, % ±SD
6	0.02	8.9±0.39	52.27±1.504	26.135 ±2.127
7	0.04	11.56±0.405	80.468±1.560	40.234 ±1.103
8	0.08	11.19±0.398	75.936±1.535	37.968± 1.919
9	0.12	11.95±0.306	85.504±1.180	42.752 ±1.689
10	0.16	12.45±0.417	92.386± 1.608	46.193± 1.143

N.B. the same expt..conditions as Table 3, but at AN/RS ratio 2/1, and temp. 50oC.

Table 4. Grafting copolymerization of AN onto RS by ammonium persulfate – bisulfite.

Expt. No.	Persulfate, %	Bisulfite, %	Nitrogen % ±SD	Polymer loading, % ±SD	Monomer conversion, %±SD
11	0.6	0.3	12.29 ± 0.354	99.033 ±1.365	49.517 ± 0.965
12	1.2	0.6	14.62 ±0.217	129.313±0.837	64.657 ±0.592
13	1.8	0.9	14.98± 0.308	136.85 ± 1.187	68.425 ±0.389
14	2.4	1.2	15.53 ± 0.401	149.385± 1.549	74.69 ± 1.095
15	3.0	1.5	15.10 ± 0.278	139.48 ± 1.072	69.740 ± 0.758

N.B. Liquor ratio 20:1, AN 2:1, for 3h at 450C .

The priority of persulfate-persulfite system is ascribed to the assumption that, for hydroxyl radicals the depolymerization of cellulose is occurred (Ogiwara and Kubota, 1968), which provide relatively higher free radicals formed on the cellulose backbone, and fast the termination step. While for persulfate-persulfite initiation, the reaction is performed as follows (Kolthoff and Meeham, 1953):

$$\begin{aligned} &S_2O_8^{2-} \longrightarrow 2SO^{\cdot -}_4 \\ &SO^{\cdot -}_4 + \text{Cell-OH} \longrightarrow \text{Cell-O}^{\cdot} \\ &SO^{\cdot -}_4 + M \longrightarrow M^{\cdot} \\ &\text{Cell-O}^{\cdot} + M^{\cdot} \longrightarrow \text{M-g-Cell} \\ &M^{\cdot} + M+. \longrightarrow \text{Homopolymer} \end{aligned}$$

To evaluate the efficiency and economical application of these grafting systems, the homopolymer-free grafted RS is determined from nitrogen content of DMF-extracted samples obtained under optimum grafting processes. The results obtained are recorded in Table 5. It is noticed that, for two studied processes lower percentages of homopolymers formed, these percentages not exceed 2.30%-3.54%. These promising results and for economical production of hydrogel, the polymerized sample as a whole (grafted sample and homopolymer), was used as the intermediate stage for preparation of hydrogels in large scale.

Effect of grafting approach on hydrogels produced (in Pilot scale)

Table 6 shows the nitrogen content of the prepared hydrogels before and after hydrolyses. The results indicate that, during alkali hydrolysis, the AN groups converted to amide and carboxylic groups (hydrophilic groups.). As can be note that, preactivation by cyanoethylation improves the formation of amide groups, whereas the reduction in nitrogen content in former case is lower than later ones.

Characterization of the prepared grafted lignocellulose and hydrogels:

IR-spectra, thermal analyses and water absorption capacity, were carried out to evidence the grafting of RS as the intermediate step to form amide-containing rice straw as hydrogel material. As well as to examine the effect of initiating system, during grafting process, and pretreating the RS, on the thermal stability of modified RS produced. The examined samples are:

- Raw RS
- PAN-g-RS (1), which was grafted under Expt. conditions # 10,
- PAN-g-RS (2), which was grafted under Expt. conditions # 14
- CE-RS, cyanoethylated RS.
- PAN-g-CE-RS(2), cyanoethylation followed by grafting under expt. Conditions #14.
- HPAN-RS(1), Alkaly hydrolysis of PAN-g-RS(1)
- HPAN-g-RS(2), alkali hydrolysis of PAN-g-RS(2)
- HPAN-g-CE-RS(2), alkali hydrolysis of PAN-g-RS(2)

FTIR-spectra

The IR-spectrum of RS (Table 7), shows characteristic bands at 3433 cm^{-1}, 2925 cm^{-1} due to OH , CH (stretching vibration) and hydrogen bonds (intra & inter molecular hydrogen bonds). The bands at 1727 cm^{-1}, 1637 cm^{-1}, corresponding to C=O (stretchning vibration); while the bands at 1441.5 cm^{-1}, 1373 cm^{-1} and 899.6 cm^{-1} corresponding to OH (bending vib.), CH (bend. Vib.) and CH (rocking vibration), respectively.

Table 5. Grafting efficiency of two initiation systems.

Expt. No.	Grating initiation system	Nitrogen % Unextracted PAN-g-RS ±SD	Extracted PAN-g-RS ±SD	Polymer loading, % ±SD	True grafting, % ±SD	Grafting efficiency,% ±SD
10	Fe^{2+}-H_2O_2 system	12.45±0.417	12.3 ±0.206	92.386 ±1.608	90.2636±0.794	97.702±1.1889
14	Per-sulfate/per-sulfite system	15.53± 0.401	14.42±0.238	149.39± 1.549	146.774±0.918	98.249±0.525

Table 6. Nitrogen content of PAN-g-RS and HPAN-g-RS prepared in pilot scale.

Samples	Nitrogen %		Polymer loading, % ±SD	Reduction in N., %±SD
	Before hydrolysis ±SD	After hydrolysis ±SD		
HPAN-g-RS (1) (Fe^{2+}-H_2O_2 system)	10.39± 0.263	8.3±0.181	66.877 ± 1.0144	19.249± 0.396
HPAN-g-RS (2) (Per-sulfate/per-sulfite system)	15.48 ±0.305	7.11± 0.186	148.1911± 1.176	54.07± 0.4196
HPAN-g-CE-RS(2), Cyanoethylation-grafting using persulfate-persulfite system)	15.51±0.223	8.11±0.1695	148.906± 0.861	47.71± 0.4822

In the IR-spectra of PAN-g-RS (1-2) samples, prepared by using the two foregoing initiating systems, under Expt. conditions # 10 and 14 (Table 7), the band maxima corresponding to stretching vibration of OH were red shifted (from 3433.6m c^{-1} to 3412 cm^{-1}, and 3420 cm^{-1}, respectively), with the appearance of a new band at 2244.7 cm^{-1}, arising from C≅N groups. This is attributed to substituting the hydroxyl groups of glucopyranose units by poly-cyanoethyl group. This group leads to diminish the intra molecular hydrogen bonds between fiber chains, as manifested from decreasing the values of MHBS and crystallinity index. The extent of decreasing MHBS values is related to the efficiency of grafting resulted from changing the initiation system.

The spectra of partially treated (RS) by cyanoethylation before grafting, using persulphate initiator (Table 7), confirm the positive effect of such treatment to improve the ability of (RS) to grafting process. Whereas, the relative absorbance of band corresponds to C≅N groups at 2444.2 cm^{-1} increased from 0.45 to 0.7023, in addition to the blue shift of the band maximum corresponds to OH (str.) from 3433 to 3444 cm^{-1}, and increased its relative absorbance and MHBS values. The reverse trends of increasing the MHBS with decreasing the degree of order (Cr. I) of pre-cyanoethylated (RS) before grafting (PAN-g-CE-RS), this is probable ascribed to the shortest of the formed propagated cyanoethyl group, than PAN-g-RS. Because, the decrystlization of cellulose containing (RS) by cyanoethylation process enhances the number of hydroxyl groups available to block with AN monomer during grafting. It can be also shown that (Figure 5), complete conversion of nitrile group to amide group, on alkali hydrolyses of PAN-g-CE-RS has not been reached, due to the remaining of C≅N band and the relative absorbance of band corresponds to C=O at 1657 cm^{-1} is lower than alkali hydrolyses of PAN-g-RS.

For the IR-measurements of modified RS-samples, Table 7-b shows that the MHBS of hydrolyzed samples are higher than those values of untreated and grafted (RS). This is ascribed to the ability of forming additional inter and intra molecular hydrogen bonding between NH of the amide groups formed with unsubstituted OH groups of glucopyranose units. The appearance of absorption bands at 1556-1564 cm^{-1} indicates the presence of COO^- together with amide groups in the hydrolyzed samples

Thermal stability

The TGA and DTG curves of unmodified RS (Figure 1 and Table 8), show three degradation stages. At lower temperature, i.e. < 112°C (1st degradation stage), the weight loss is due to the evolution of sorbed moisture. The second process, in the range from166-328°C is due to the decomposition of RS components, leading to the formation of carbonaceous char. This is followed by weight loss within the temperature of 328-484°C due to oxidation of charred product (Shafizadeh, 1982). The 2nd and 3rd process regard the main degradation stages.

For PAN-g-RS (1 and 2), the start temperature of the 2nd degradation stages are higher than ungrafted RS. This is due to the blocking of hydroxyl group by poly-AN-groups. As can be noticed that, maximum raise in the start temp. was noticed for PAN-g-RS(1) than PAN-g-RS(2), this is ascribed to the fact that during free radical copolymerization process, the trunk polymer is depolymerized, which leads to scission of chains (Yoshitaka et al., 1968). This effect is more observed at relatively higher grafted RS (PAN-g-RS(2)).

Table 7-a. Main IR-absorption bands and IR-measurements of un- and modified rice straw.

a- Main IR-absorption bands.

Sample	ν_{OH} or ν_{NH} (stretching)		ν_{CH} (stretching)		$\nu_{C\equiv N}$ (stretching)		$\nu_{C=O}$ (stretching)		ν_{OH} or ν_{NH} (bending)		ν_{CH} (rocking)	
	cm^{-1}	E	cm^{-1}	E	cm^{-1}	E	cm^{-1}	E	cm^{-1}	E	cm^{-1}	E
Rice straw	3433.6	0.9923	2925	0.7544	-	-	1727	0.5667	1426	1.1685	896.7	0.4539
							1637.3	0.9372				
PAN-g-RS (1)	3412	1.1279	2925	0.9492	2244.7	0.5915	1724	0.6468	1450	1.143	890	0.2147
							1658.5	0.8998				
PAN-g-RS (2)	3420	0.9584	2926	0.9954	2244.7	0.4597	1659	1.016	1447.3	1.2852	902.5	0.2280
			2880.17	0.7177								
CE-RS	3431	1.3106	2927.4	1.0599	2267.9	0.3551	1665	0.6695	1443.5	0.7275	926.6	0.3221
			2886.9	0.9278			1635.3	0.7326				
PAN-g-CE-RS	3444.2	1.3709	2928.4	1.1547	2247.6	0.70236	1729.8	0.3982	1451.2	0.8641	895.77	0.4307
			2895.6	0.9124			1665.23	0.8739				
							1638.2	0.7815				
HPAN-g-RS (2)	3446.2	3.3858	2928.4	1.4099	-	-	1643.1	1.8345	1432.9	2.452	879.4	0.4667
			2850.3	0.7824			1556.3	1.6299				
HPAN-g-CE-RS (2)	3451.9	2.2021	2929.3	1.1309	2253.4	0.37697	1657.5	1.2434	1460.8	0.8335	874.6	0.3558
			2862.8	0.8099			1564.95	1.2101	1412.6	0.9637		

Table 7-b. IR-Measurements.

Sample	MHBS ($A_{OH(Str.)}/A_{CH\ (Str.)}$)	Cr.I. ($A_{\sim 1370\ cm^{-1}}/A_{\sim 2920\ cm^{-1}}$)
Rice straw	1.3154	1.248
PAN-g-RS (1)	1.1442	1.062
PAN-g-RS (2)	0.96285	1.079
CE-RS	1.2365	0.704
PAN-g-CE-RS	1.1873	0.697
HPAN-g-RS (2)	2.40143	0.774
HPAN-g-CE-RS (2)	1.9472	0.623

Table 8. Kinetic parameters of un- and modified rice straw.

Sample code in chart	stage	Temp. range °C	DTG peak temp. °C	"n"	-r	Se	E_a kJ/ mole	Wt. (final)
Rice straw	1st	50- 112.03	62.57	-	-	-	-	19.045
	2nd	166-327.5	254.07	1.0	0.99498	0.07634	79.365	
	3rd	327.5-484.2	439.65	1.0	0.98895	0.06945	91.948	
							Σ Ea = ١٧١ .٣١٣	
PAN-g-RS (1)	1st	50- 110.1	62.57	-	-	-	-	5.951
	2nd	208.6-273.4	257.4	0.5	0.9811	0.1515	188.4999	
	3rd	351.9- 610	527.4	0.5	0.8974	0.2085	61.674	
							Σ Ea = 250.17	
PAN-g-RS (2)	1st	50- 106	67	-	-	-	-	5.188
	2nd	197.4 – 358.2	249.1	1.5	0.9752	0.2009	122.286	
	3rd	407.4 - 686.6	575	1.0	0.9643	0.1605	97.648	
							Σ Ea = 219.934	
HPAN-g-RS (2)	1st	50- 147.9	85.2	-	-	-	-	12.839
	2nd	249.1 -298	286.3	1.0	0.9477	0.2155	255.19	
	3rd	298.1-340.5	320.6	1.0	0.9594	0.1914	369.16	
	4th	516 -611	564.4	1.5	0.9910	0.1386	508.62	
							Σ Ea = 1132.97	
HPAN-g-CE-RS (2)	1st	50- 100	86.5	-	-	-	-	24.443
	2nd	245.9 -356	338.1	1.0	0.9398	0.241	134.01	
	3rd	356 -387.8	382.3	0.0	0.9599	0.1874	793.05	
	4th	493.2 – 529.9	515	1.5	0.9873	0.1905	1074.89	
							Σ Ea = 2001.95	

TG and DTG curves of alkali-hydrolyzed of grafted samples (HPAN-g-RS and HPAN-g-CN-RS); Figure 2, show increased in onset temperature than grafted RS. This is attributed to the formation of amide and carboxylic groups (NH and C=O groups), which consequently enhances the formation of intra molecular hydrogen bonding with hydroxyl groups, in other glucopyranose units. Therefore, more energy is needed for decomposition (Table 8). This view confirms the increase in MHBS and Cr. I in the case of hydrolyzed samples than unhydrolyzed grafted samples.

Table 8 also shows that, thermal stability of the foregoing examined samples increase in the order:

HPAN-g-CN-RS > PAN-g-RS (2) > PAN-g-RS (1) > PAN-g-RS (3).

Effect of grafting approach on water absorption capacity

This work was carried out as a preliminary study to evaluate the role of grafting process and type of acid used to adjust the pH-value of the produced hydrogels with high water absorption for both distilled and Nile water. The examined hydrogel samples and their water absorption are listed in Table 9.

Table 9 shows that, the increase in the hydrophilic group (COOH) together with the amide groups, as the case of HPAN-g-RS, using persulfate-persulfite initiation system, led to increase its ability to absorbs more quantity of water than HPNA-g-RS Fe(II)-H_2O_2). Also, while cyanoethylation was taken place, some carboxyl groups is formed, this causes to improve the water absorption ability of hydrogel HPAN-g-CE-RS produced.

Generally the water absorption capacities of investigated hydrogels in the case of distilled water are higher than Nile water; this may be ascribed to the high affinity of these hydrogels to bind sodium ions in Nile water, which leads to restrict, to some extent, the swelling behaviour of hydrogels in water. As can be noticed that samples # 1 # 4, # 8 and #10 have the best water absorption property. These samples will be used for the further studies, on evaluation of the prepared hydrogels in agronomic applications under laboratory and green house conditions:

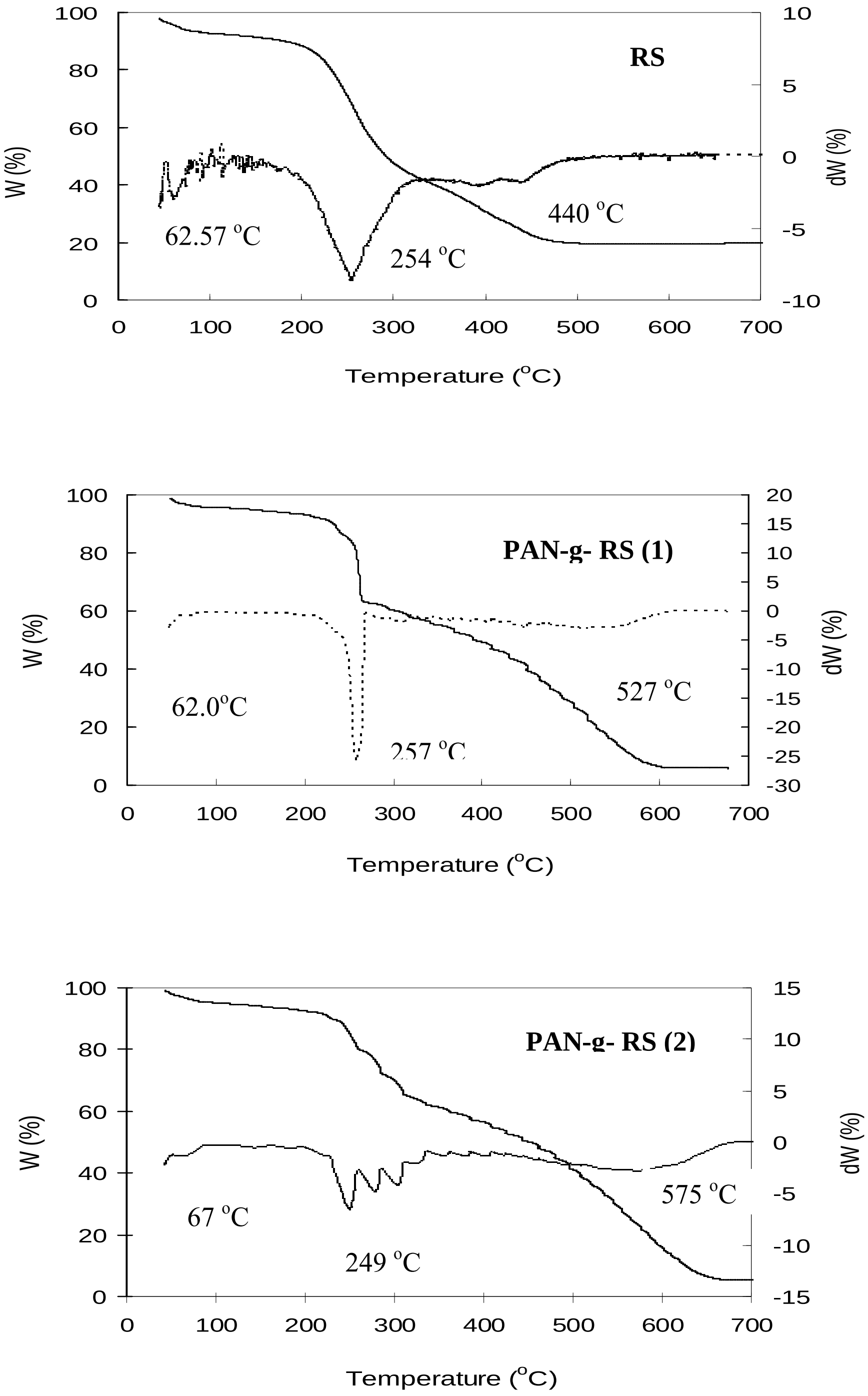

Figure 1. TGA and DTG curves for RS and PAN-grafted RS.

Table 9. Water absorption capacities of hydrogels produced.

Sample No.	Hydrogel	Used acid	Absorption capacity Sat/Dry x١٠٠	
			Distilled water ±SD	Nile Water ±SD
1	HPAN-g-RS (1)	AcOH	6710.4± 17.13	6107.0± 15.556
2	HPAN-g-RS (1)	H_2SO_4	1522.6± 9.637	875.8± 20.082
3	HPAN-g-RS (1)	H_3PO_4	1366.2± 14.425	935.8± 22.345
4	HPAN-g-RS (1)	HNO_3	3318.2± 5.375	2024.7± 20.784
5	HPAN-g-RS (2)	AcOH	2121.9± 18.246	2602.5± 6.364
6	HPAN-g-RS (2)	H_2SO_4	1238.3± 8705	1441.7± 15.981
7	HPAN-g-RS (2)	H_3PO_4	991.9± 10.041	663.9± 8.627
8	HPAN-g-RS (2)	HNO_3	3008.1± 8.414	3128.2± 24.142
9	HPAN-g-CE-RS (2)	H_3PO_4	2403.4± 3.820	1907.1± 21.113
10	HPAN-g-CE-RS (2)	AcOH	7061.4± 11.594	3788.7± 23.517
11	HPAN-g-CE-RS (2)	HNO_3	2794.7± 12.104	1822.1± 14.2846
12	HPAN-g-CE-RS (2)	H_3PO_4 +HNO_3	2166.7± 13.007	2639.5 ± 16.775

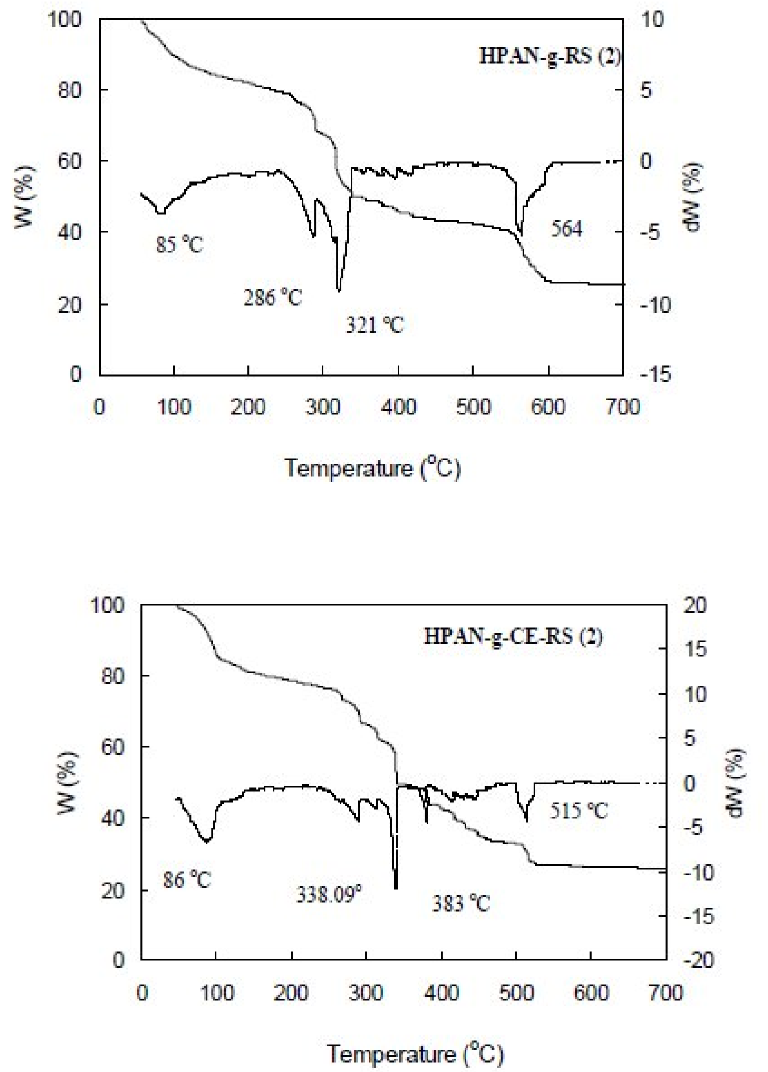

Figure 2. TGA and DTG curves for hydrolyzed PAN-grafted RS.

Table 10. Toxicity test for the effect of the prepared hydrogels on the most beneficent microorganisms in the soil.

Examined hydrogel	*Rhizobia sp*.					*Azotobacter sp.*	*Azospirillum* sp.	*Bacillus suptlis*	Phosphate dissolving bacteria	*Actino-micites*	Fungi
	Alfa-alfa	*Clover*	*Broad bean*	*Peanut (T110)*	*phasoleai*						
Gel #1	--	--	--	--	--	--	---	----	---	--	----
Gel # 2	---	---	---	---	---	---	----	----	----	---	---
Gel # 3	--	--	--	--	--	--	----	----	---	---	---
Gel # 4	----	----	----	----	----	----	---	----	----	---	----

* Affected area around the polymer.

-- 10-15% --- 5-10% ---- <5%.

Toxicity (inhibitory) test against the most efficient micro-organisms in plants media (rizosphere).

This study was carried out on the following canditated hydrogels, taking into consideration that the concentration of applied hydrogels in petri dishes are higher than that normally used in soil conditioning .

Gel #1, was prepared under expt. Conditions (0.12 H_2O_2/RS ratio, 0.1% ferrous ammonium sulfate, 2AN /RS, for 3 h, at 50°C followed by alkali hydrolysis), using AcOH for neutralize the pH-value to ~ 6-7

Gel #2, was prepared under expt. Conditions (0.12 H_2O_2/RS ratio, 0.1% ferrous ammonium sulfate, 2AN /RS, for 3 h, at 50°C followed by alkali hydrolysis), using HNO_3 for neutralize the pH-value to ~ 6-7

Gel #3, was prepared under expt. Conditions (1.8% persulfate, 0.9% bisulfite, 2AN/RS ratio, for 3 h, at 45°C, followed by alkali hydrolysis), using HNO_3 for neutralize the pH-value to ~ 6-7.

Gel #4, was prepared by grafting the partially cyanoethylated RS, under the same conditions of hydrogel # 3, using AcOH for neutralize the pH-value to ~ 6-7.

Data presented in Table 10 are mean of three replications (four pieces/each plate=12 determinations). These data indicate that the prepared hydrogels having no-toxic effect for most of the beneficent micro-organisms in plant rhizosphere, and they can be safely used as soil conditioners. Gels no. 2 and no. 4 may be prepared to be used for most crops; while gels # 1 and # 3 can be used with crops except legumes.

Conclusion

From all the foregoing results it could be concluded that, the approach of grafting had a significant effect on water absorption affinity of the hydrogels produced. Whereas, using Ferrous sulfate-H_2O_2 initiation system rendered hydrogel with a relatively higher absorption capacity towards both distilled and Nile water than using persulfate-persulfite initiation system. Precyanoethylation of RS, especially on using AcOH for adjusting the pH of hydrogel, promoted the utilization of persulfate-persulfie initiation system (adsorption capacity increased from 2602.5 to 3788.7 for Nile water and from 2121.9 to 7061.4 for distilled water). These hydrogels have no-toxic effect for most of the beneficent micro-organisms in plant rhizosphere, and they can be safely used as soil conditioners.

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References

Abdel-Hameed, E. S., H. A. El-Nahas and S. A. Abo-sedera. 2008. Anti-schistosonal and antimicrobial activities of some Egyptian plant species. Pharm. Biol. 46(9):626-633.

Ansel, C. W. G. 1995. New synthetic hydrogels. Macromol. Rep. A32:733-739.

Athawale, V. D. and V. Lele. 2000. Syntheses and characterisation of graft copolymers of maize starch and methacrylonitrile. Carbohydr Polym. 41:407–416.

Bains, M. S. 1972. Inorganic redox systems in graft polymerization onto cellulosic materials. J.Polym. Science Part C: Polymer Symposia, 37(1):125–151.

Basta, A. H. 1999. Preparation, characterization and properties of paper sheets made from chemically modified wood pulp treated with metal salts Int. J. Polym. Mat. 42:1-26.

Buchholz, F. L. and N. A. Peppas. 1994. Superabsorbent Polymer Science and Technology, American Chemical Society, Washington, DC, p.123.

Burr, R. P., G. F. Fanta, W. M. Doane and C. R. Russell. 1976. Graft copolymers of starch and mixtures of acrylamide and acrylic acid. J. Appl. Polym. Sci. 20:3201-3204.

Coat, A. W. and J. P. Redfern. 1964. Kinetic parameters from thermogravimetric data. Nature 201(4914):68-72.

El-Saied, H., A. I. Waly and A. H. Basta. 2000. Highly water absorbents from lignocelluloses. Polym. Plastic Technol. Eng. 39:905-926.

El-Saied, H., A. I. Waley, A. H. Basta and O. El-Hadi. 2004. Water Absorbents from Lignocelluloces: Novel Soil Conditioners of Sandy Soil from Lignocellulosic Wastes. Polym. Plastic Technol. Eng. 43(3):777-795.

El-Saied, H., A H Basta, O. El-Hadi and A. I. Waley. 2007. High Water Absorbents from Lignocelluloses. Pt. III: Upgrading the Utilization of Old News Paper (ONP) in Agronomic Applications. Plast. Polym.

Technol. Eng. 46 (3): 311-319.

Fanta, G. F., R. C. Burr and W. M. Doane. 2006. Factors influencing absorbent properties of saponified starch-g-polyacrylonitrile isolated by methanol precipitation. Starch-Stärke 36(12):416-419.

Fanta, G. F. and W. M. Doane. 1990. Advances in carbohydrates chemistry. ACS Symp. Ser. 433:288-303.

Jayme, G. and P. Sarten. 1940. Uber die quantitative Bestimmung von Pentosenmittels Bromwasserstoffsaure. Naturewissenchaften 28(52):822–23.

Karlsson, J. O., A. Henriksson and P. Gatenholm. 2000. Control of cellulose-supported hydrogel microstructures by three-dimensional graft polymerization of glycol methacrylates. Polymer 41(4):1551-1559.

Kennedy, J. K., G. O. Philips and P. A. Williams. 1993. Cellulosics: Chemical Biochemical and Material Aspects, Ellis Horwood, London, p.391.

Kolthoff, I. M. and J. E. Barney. 1951. Cataltic polarographic waves of hydrogen peroxide. I. The kinetic wave for the ferric ion-hydrogen peroxide system. J. Amer. Chem. Soc. 73:3718-3723.

Kume, T., N. Nagasawa and F. Yoshii. 2002. Utilization of carbohydrates by radiation processing. Rad. Phys. Chem. 63(3-6):201-850.

Levdik, I., M. D. Inshakov, E. P. Misyurova and V. N. Nikitin. 1967. Study of pulp structure by infra-red spectroscopy.Tr. Vses Nauch. Issled. Irst. Tsellyul Bum. Prom. 52:109-111.

Li, X. and X. Pan. 2010. Hydrogels based on hemicellulose and lignin from lignocellulose biorefinery: a mini-review. J. Biobased Mat. Bioen. 4(4):189-297.

Markblatt IV/29 Zellcheming (Germen Association of cellulose chemist & Engineering).

O'Connor, R. T., E. F. Du Pre and D. Mitchoum. 1958. Applications of infra-red absorption spectroscopy to investigations cotton and modified cotton, Pt. I. Textile Res. J. 28:382-389.

Ogiwara, Y. and H. Kubota. 1968. Studies of the initiation mechanism of ferric ion–hydrogen peroxide systems in graft copolymerization on cellulose. J. Appl. Polym. Sci. 12:2575 -2584.

Saito, N., K. Seki, M. Aoyama.. 1991.Super-absorbent materials prepared from lignocellulosic materials by phosphorylation. Sen-1Gakkaishi 47:255-258.

Saito, N., M. Aoyama, Y. Shimizu, M. Takai and J. Hayashi. 1995. Super-absorbent materials prepared from lignocellulosic materials by phosphorylation VI. Swelling and morphological changes. Mokuzai Gakkaishi 41:179-183.

Shafizadeh, F. 1982. Introduction to pyrolysis of biomass. J. Anal. Appl. Pyrol. 3:283-305.

Singh, V., P. Kumar and R. Sanghi. 2012. Use of microwave irradiation in the grafting modification of the polysaccharides–A review. Progr. Polym. Sci. 37(2):340-364.

The Institute of Paper Chemistry, 1951. Institute Method No. 428. Institute of Paper Chemistry, Appleton, Wisconsin.

Yoshitaka, O., O. Yukie and K. Hitoshi. 1968. Copolymerization of acrylonitrile-cellulose and properties of superabsorbents. J. Appl. Polym. Sci. 12:2375-2381.