Synthesis and application of lignin-based copolymer LSAA on controlling non-point source pollution resulted from surface runoff

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Abstract

In this article, alkali lignin separated from paper pulp waste was grafted into a novel copolymer LSAA (a copolymer of lignin, starch, acrylamide, and acrylic acid). Its practical application effect and environmental safety were studied. The results of field simulation experiment indicated that the application of LSAA significantly affected the output of the runoff and pollutants. The runoff quantity was decreased by 16.67%–47.00% and the loads of total suspended solids (TSS), chemical oxygen demand (COD), total nitrogen (TN), and total phosphorus (TP) were reduced by 17.78%–62.14%, 26.32%–59.91%, 15.25%–47.42%, and 22.18%–52.78%, respectively. The tests on its environmental safety showed that LSAA did no harm the soil. Compared with polyacrylamide (PAM), a dominant product in this field, LSAA exhibited similar effects and cheap cost. Thus, this study not only created a new product for controlling runoff water quality but also offered a beneficial application for industrial paper waste.

Key words: application; copolymer; a copolymer of lignin, starch, acrylamide and acrylic acid (LSAA); non-point source pollution (NPS); surface runoff

Introduction

Non-point source pollution (NPS) originated from surface applied chemical in either liquor or solid form is caused by rainfall. Now it is the primary source of water contamination in rivers, lakes, and streams (Cang and Xu, 2005). However, NPS is difficult to be controlled because of the diffuse pollutant source. In China, the problem is complicated for the vast territory and the multiplex types of landuse. Thus, how to control and manage NPS has become a essential issue for researchers in the last two decades.

Best Management Practices (BMPs) issued from Environmental Protection Agency (USEPA) is considered to be the most efficient management program on controlling NPS till now, which calls for the development of new techniques if they are proved to be efficient for a certain area (Young and Karkoski, 2000). The application of polymers on reducing surface runoff contamination was proved to be a feasible way to control NPS. From the early 1990s, polyacrylamide (PAM) was used as an effective strategy to control soil erosion (Lentz and Sojka, 1994) and to protect water quality threatened by agricultural runoff contaminations (Entry *et al.*, 2002). The successful use of PAM drove the development of the polymers with

similar properties, such as cellulose, starch xanthates, and chitosan (Meadows, 1956; Meadows, 1959; Swanson *et al.*, 1975; Menefee and Hautala, 1978; Maher, 1981). Although these polymers were able to reduce soil erosion and to protect surface water from sediments and other contaminants washed from eroding field, they were unideal due to their high cost and the environmental safety concerns. Hence, the exploration of economical, applicable, and environmental safe polymer products is still one of the challenging issues.

Environmental concerns related to waste disposal have encouraged the design of biodegradable materials and provided the driving force to find new usage for by-products generated by industrial processes (Corradini *et al.*, 1999). Lignin, as a major by-product in the paper-making industry, is generally discharged into rivers rather than recycled and reused because of the lack of and inefficiency of alkali recycling. Every year up to 5×10^7 t lignin are produced and disposed of as waste. It not only wastes resources but also brings up serious aquatic environmental contamination (Zhang and Chuang, 2001). On the other side, lignin has been considered as an enormous and inexpensive raw natural material. Its natural macromolecule structure is composed of phenoylpropane units, connected by various types of linkages, thus forming a branched structure owning diverse functional groups (Carsten *et al.*, 2000). It has been widely used in different aspects around

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the world, such as animal bypass protein, gypsum board additives, ceramic additives, industrial dust suppressant, dyestuff, agro chemicals, water treatment dispersants and so on. Recently, some researchers applied lignin and its polymer on the protection of water and soil (Wang *et al.*, 2005; Wei *et al.*, 2000). However, little research has been done on the lignin-based product application controlling NPS (Mu *et al.*, 2006).

The objectives of the study are to introduce a new method for NPS control and point a beneficial application for industrial by-product lignin. It offers a feasible way to resolve the contradiction between environmental protection and economic demand to a certain extent.

1 Materials and methods

1.1 LSAA manufacturing

LSAA is a new multi-components copolymer made from lignin, starch, acrylamide, and acrylic acid by the way of radical polymerization. The tested lignin was produced by a papermaking company in Shandong Province of China, retrieved from black papermaking liquid of alkali system with acidifying. The content of water and ash was 3% and 6%, respectively. Other reagents were commercial products from Shuangxiangda Experimental Material Co., Ltd. (Beijing, China), and were all of analytical grade.

The reaction was carried out in a 250-ml glass reactor equipped with various access ports capable of accommodating addition funnel, thermowell, and pH meter probe. In a typical reaction, 2 g lignin sample, 0.2 g starch, 8 g acrylamide, and 6 ml acrylic acid ($\rho = 1.05 \text{ g/ml}$) were charged into the reactor with distilled water. The solution pH was adjusted to 7.5 with NaOH. The solution volume was kept 100 ml with distilled water. And the mixture was stirred slowly and meanwhile heated to 70°C with the protection of nitrogen gas for 0.5 h. Then 0.6 g potassium persulfate was added to initiate the reaction and the mixture was continuously stirred for a period. Both pH and temperature were monitored during the reaction. Finally, the product LSAA was extracted by acetone from the mixture and then dried to constant weight at 60°C .

For LSAA characterization, fourier transform infrared (FT-IR) spectra were gained using U-3100 spectrophotometer (Ultraviolet vision, Hitachi, Japan). The produced LSAA was well grounded and dispersed in KBr to form pellets and spectra were recorded in the range of $\nu_{\max}$ $4,000\text{--}500 \text{ cm}^{-1}$.

1.2 Soil property

The tested soil was obtained from Hanyang district in Wuhan city of Hubei Province in China, which is located between $114.3^\circ\text{--}114.17^\circ\text{E}$ and $30.25^\circ\text{--}30.36^\circ\text{N}$. Red-clay is the representative kind of soil in the district. It readily forms soil seals and crusts at the surface on impact of raindrops, which can significantly reduce the soil infiltration rate and increase runoff. The soil properties were analyzed according to the methods by Lu (2000). The results are shown in Table 1.

Table 1 Soil properties

Parameter	Value
Humus content (%)	2.34
Water content (%)	3.35
pH	5.58
Organic matter (%)	3.38
Total N (TN) (%)	0.28
Total P (TP) (%)	0.09
Sand (%)	12.0
Silt (%)	39.4
Clay (%)	48.6
CaCO_3 (%)	0.43

1.3 Study on the infiltration-enhancing effect

The air-dried soil eliminated weeds and stones were passed through a 2-mm sieve, and then put into the designed containers; meanwhile, the bulk density of the tested soil was kept consistent. As planned, a certain dose of the LSAA solution has been sprinkled onto the soil surface. After the treated soil has been incubated for 3 d, the infiltration coefficient (K) was measured by means of infiltration canister (Lu, 2000).

All results were expressed on an oven-dry soil basis (105°C , 24 h) and the mean of three replicate analyses was used in this study.

1.4 Field simulation experiment

The field experiment was conducted in the Research Center for Eco-Environmental Science, Chinese Academy of Sciences, in Beijing, China. It was designed for two aims: (1) to test the effect of LSAA on the runoff flow and pollutant loads under the condition of rainfall simulation; (2) to compare the effect of LSAA with that of PAM.

In the experiment, three treatments and replications of each treatment were arranged. Each treatment was 84 cm, 300 cm, and 50 cm in width, length, and depth, respectively, with the slope of 5% (Fig. 1). And the soil bulk density of each treatment was kept consistent. LSAA and PAM were dissolved into distilled water for use. First, the treatments of LSAA and PAM were sprayed by 3 kg/hm^2 LSAA and 3 kg/hm^2 PAM, meanwhile the controlled trial was sprayed by the same amount of water instead. After a week of incubation, the simulation rainfall experiment was started. The prepared artificial rainfall water was of 180

Fig. 1 Sketch of field experiment under rainfall simulation.

mg/L COD, 27 mg/L TN and 1.2 mg/L TP by mixing the proper dosage of glucose, NH_4Cl , KNO_3 , and KH_2PO_4 . The process of rainfall was simulated and controlled by water pump. Each treatment was designed to get the same amount of rainfall water but different rainfall intensity. Through altering the pump power, three levels of rainfall intensity, 36, 72, and 108 mm/h, were achieved. Thus the rainfall process lasted 45, 23, and 15 min, respectively. During the test, runoff flow from each treatment was continuously monitored and water samples proportional to the flow were collected.

Runoff samples were collected within less than 1 h after the end of an event. A portion of each sample was filtered through a 0.45-mm pore diameter Millipore filter to remove suspended particles while the other portion was left unfiltered. Samples were stored at 4°C and analyzed for sediment and nutrient content. Sediment loss from plots was estimated by quantitatively weighing the sediment collected within each runoff sample after oven drying at 105°C for 24 h. The samples were analyzed for total suspended solids (TSS), COD_{Cr} , TN, and TP according to the Chinese Standard Methods (EPA of China, 2002).

1.5 Microbiological analysis

In this study, soil respiration and the activities of urease were adopted to test the environmental biologic effect of LSAA.

Soil respiration was determined as reported by Anderson and Domsch (1978). This analytic method was based on the determination of CO_2 evolved from undisturbed soils. NaOH solution 1 mol/L was placed in an open glass jar above the soil surface and the jar was sealed. After 24 h of incubation, the NaOH solution was removed and the trapped CO_2 was titrated with HCl.

Urease activity (UA) was measured using the method by Hoffmann and Teicher (1961). A 7.5-ml citrate buffer (pH 6.7) and 10 ml of 10% urea substrate solution were added to 10 g of dry soil, and the samples were incubated for 3 h at 37°C. The volume was kept at 100 ml with distilled water at 37°C. Following filtration through filter papers, 1 ml of filtrate was diluted to 10 ml with distilled water, and 4 ml of sodium phenolate (12.5% (W/V) phenol + 5.4% (W/V) NaOH), and 3 ml of 0.9% sodium hypochloride were added. The released ammonium was determined spectrophotometrically at 578 nm.

All the results were expressed on an oven-dry soil basis (105°C, 24 h) and were the mean of three replicate analyses.

2 Results and discussion

2.1 Fourier transform infrared (FT-IR) spectroscopic measurements

In this study, $-\text{CONH}$ and $-\text{COO}^-$ were grafted onto the native lignin and the infrared spectroscopy of the copolymer LSAA is shown in Fig.2. The important peaks at 1,120 and 2,930 cm^{-1} were assigned to lilac aromatic ring framework and methylene, which were the characteristic

groups of lignin molecular structure. And the characteristic peaks at 1,680 and 1,450 cm^{-1} demonstrated $\text{C}=\text{O}$ and $\text{N}-\text{H}$ deformable vibration adsorption, respectively. Those indicated the existence of $-\text{CONH}$. Besides, the characteristic peaks at 1,560 cm and 1,410 cm^{-1} were as signed to $-\text{COO}^-$.

2.2 Effect of LSAA on infiltration-enhancing

As Fig.3 shows, the application of LSAA significantly influenced the soil infiltration coefficient (K_{10}) and the positive relationship of K_{10} with the LSAA dosage was observed. In the entire test, K_{10} was elevated by 10.56%–32.27% and it increased with increasing LSAA dosage. When the dosage increased from 1 to 3 kg/hm^2 , adding 1 kg/hm^2 LSAA average elevated K_{10} by 5%. However,

Fig. 2 Infrared spectrum of LSAA (a copolymer of lignin, starch, acrylamide and acrylic acid).

Fig. 3 Soil infiltration coefficient K_{10} of various LSAA dosage.

Table 2 Runoff output by the treatment of LASS or PAM

Run	Runoff output (ml/(min·m ²))		
	Control	LSAA	PAM
1	17 ± 1 a	15 ± 2 a	10 ± 1 b
2	217 ± 10 a	124 ± 9 b	90 ± 10 c
3	218 ± 4 a	146 ± 2 b	134 ± 10 b
4	1358 ± 64 a	1011 ± 54 b	974 ± 40 b
5	1544 ± 15 a	1102 ± 55 b	1080 ± 74 b
6	1513 ± 45 a	1213 ± 77 b	1109 ± 104 b
7	4603 ± 216 a	3581 ± 136 b	3358 ± 242 b
8	4616 ± 68 a	3147 ± 275 b	2840 ± 238 b
9	4675 ± 160 a	3646 ± 100 b	3019 ± 104 c

PAM: polyacrylamide. Run 1, 2, 3 were carried out under the rainfall intensity of 36 mm/h, run 4, 5, 6 were carried out under the rainfall intensity of 72 mm/h, run 7, 8, 9 were carried out under the rainfall intensity of 108 mm/h. Values are mean ± SD. Means within a row followed by the same letter are not significantly different ($P > 0.05$).

when the dosage increased from 3 to 6 kg/hm², adding 1 kg/hm² LSAA average elevated K_{10} by only 2%. Thus, with the consideration of both economy and efficiency, the dosage of 3 kg/hm² was adopted.

2.3 Effect of LSAA on runoff

2.3.1 Runoff output

Runoff output volumes varied with the different treatments as shown in Table 2. The statistics results indicated the field application of LSAA significantly affected the runoff output. In the experiment, the runoff output was reduced by 16.67%–47.00%. When the rainfall intensity was 36, 72, and 108 mm/h, the average runoff output reduction rates were 31.93%, 24.67%, and 25.26%, respectively. And under the rainfall intensity of 36 mm/h, the application of LSAA showed stronger ability to reduce the runoff output volume compared with the situations under the intensities of 72 and 108 mm/h. It indicated that small rainfall intensity was beneficial for LSAA to exert the effect on runoff reduction.

Several factors, such as surface soil physical properties, root channels, soil cracks, and micro-fauna activity influence surface runoff. In addition, soil texture plays the most dominant role (Nyakatawa *et al.*, 2006). LSAA with macromolecular structure and several various functional groups obtains an affinity to charged soil particles. By the way of spraying it onto the soil surface, it is able to strengthen the soil granule reuniting each other and to promote the formation of soil aggregates. The changes of these microcosmic states enlarged the degree of soil pore. Then the soil infiltration coefficient increased which accelerated the speed of rainfall infiltration and reduced the runoff output volume.

2.3.2 Pollutants in runoff

TSS is a measure of the concentrations of sediment, solid particles suspension and other pollutants carried by runoff, because nutrients, metals, and organic compounds are typically attached to sediment particles (Vieux and Moreda, 2003). In the test, the TSS concentration and loads were affected significantly by the application of LSAA (Table 3). Those were reduced by 2.82%–45.11% and 17.78%–62.14%, respectively. In the entire event, the TSS concentration and loads obviously varied with the different rainfall intensities and increased with the rainfall intensity enhancing. When the rainfall intensity was 36, 72, and 108 mm/h, the TSS concentration was cut down by 4.67%, 24.47%, and 43.33%, and the TSS loads were cut down by 34.13%, 42.98%, and 57.38%, respectively. Moreover, stronger rainfall induced more soil loss. Meanwhile, the function of LSAA also varied with the different rainfall intensities. Those showed that it would be more significant for LSAA to reduce TSS under larger rainfall intensity.

The COD_{Cr} is one of the important indices to indicate water quality. As Table 4 shows, the COD_{Cr} concentrations and loads were significantly reduced by the treatment of LSAA. Where, the COD_{Cr} concentration was reduced by 10.29%–26.07%, and COD_{Cr} loads were reduced by 26.32%–59.91%. When the intensity was 36 mm/h, 72

mm/h and 108 mm/h, it was cut down by 23.83%, 14.99% and 25.54%, respectively. And as for the total COD_{Cr} loads, it was reduced on average by 36.11%, 30.33% and 45.11%, respectively.

The results of TN and TP are shown in Tables 5 and 6. The treatment of LSAA could not significantly effect the concentration of TN and TP, but significantly reduce their total output. When the rainfall intensity was 36, 72, and 108 mm/h, TN loads were cut down by 28.94%, 23.38%, and 30.98%, and TP loads were cut down by 31.20%, 23.98%, and 30.42%, respectively. The output of TN and TP were greatly affected by the rainfall intensity. They increased with the rainfall intensity enhancing. However, the same trend did not occur on the function of LSAA. Under various rainfall intensities, the differences were small.

2.3.3 Comparison between LSAA and PAM

PAM is a typical soil additive to prevent erosion and enhance infiltration. In the experiment, PAM was considered to be a comparison with LSAA. The results indicated that PAM could significantly reduce the output of runoff, TSS, COD_{Cr}, TN, and TP (Tables 2–6), which was consistent with the conclusion of many correlative studies (Lenze and Sojka, 1994; Lentz *et al.*, 1998; Entry *et al.*, 2002). The data of the comparison between LSAA and PAM indicated no significant difference.

2.4 Effect of LSAA on environmental biology

Even though being highly effective in reducing the pollutants, a product still should not be commended to use if it is harmful to the ecological environment. To evaluate environment safety, microbiological index has been broadly accepted as a convincing measurement.

Soil respiration is one of the most important indexes of the soil microbiology. It was found to be mainly associated with the microbial population and activity (Rochette *et al.*, 1991), and also closely associated with the soil physical and chemical properties. As Table 7 shows, in the first four days, the addition of LSAA affected the soil respiration significantly. The CO₂ emission increased 8.6%–12.8% on average. It indicated that the microbe was stimulated by the addition of LSAA in the beginning. It may be because the addition of LSAA not only altered the physical properties of soil but also offered a kind of new source of C and N for the soil original microbe, which would change the microbial population. However, during the following days no significant difference was observed. It may be due to the formation of new microbial predominant community adapted to the new soil additive (Zheng *et al.*, 2007). As for urease activity (Table 8), no significant difference due to various treatments was observed during the first four days. Then in the following week, the results indicated that the application of LSAA significantly reduced the urease activity. In contrast, during day 12 to 15, the urease activity presented increased with increasing LSAA dosage. The results indicated that the application of LSAA could decrease the urease activity first and then increase it.

The results of this experiment did not indicate any

Table 3 Total suspended solid (TSS) concentration and loads by the treatment of LSAA or PAM

Run	Concentration ($\times 10^{-1}$ g/(L·min·m ²))			Loads ($\times 10^{-2}$ g/(min·m ²))		
	Control	LSAA	PAM	Control	LSAA	PAM
1	2.52 ± 0.24 a	2.37 ± 0.08 a	2.02 ± 0.39 a	0.045 ± 0.007 a	0.037 ± 0.006 a	0.020 ± 0.006 b
2	1.41 ± 0.07 a	1.38 ± 0.10 a	1.05 ± 0.10 b	0.31 ± 0.03 a	0.16 ± 0.02 b	0.16 ± 0.08 b
3	1.53 ± 0.28 a	1.45 ± 0.15 a	1.38 ± 0.05 a	0.33 ± 0.06 a	0.21 ± 0.02 b	0.18 ± 0.01 b
4	2.39 ± 0.26 a	1.66 ± 0.09 b	0.94 ± 0.07 c	3.23 ± 0.20 a	1.67 ± 0.07 b	0.91 ± 0.09 c
5	1.66 ± 0.12 a	1.25 ± 0.16 b	1.21 ± 0.05 b	2.56 ± 0.16 a	1.39 ± 0.24 b	1.30 ± 0.07 b
6	1.21 ± 0.12 a	0.99 ± 0.05 b	0.82 ± 0.14 b	1.84 ± 0.23 a	1.20 ± 0.13 b	0.91 ± 0.09 c
7	4.76 ± 0.61 a	2.63 ± 0.85 b	2.51 ± 0.22 b	21.76 ± 1.79 a	9.47 ± 3.41 b	8.39 ± 0.49 b
8	3.48 ± 0.41 a	1.91 ± 0.30 b	1.95 ± 0.14 b	16.03 ± 1.66 a	6.07 ± 1.46 b	5.57 ± 0.83 b
9	3.29 ± 0.39 a	1.97 ± 0.31 b	1.90 ± 0.43 b	15.42 ± 2.35 a	7.17 ± 0.94 b	5.72 ± 1.09 b

Runs 1–9 are the same as that in Table 2. Values are mean ± SD. Means within a row followed by the same letter are not significantly different ($P > 0.05$).

Table 4 Chemical oxygen demand (COD_{Cr}) concentration and loads by different treatment of LSAA or PAM

Run	Concentration (mg/(L·min·m ²))			Loads (mg/(min·m ²))		
	Control	LSAA	PAM	Control	LSAA	PAM
1	10.87 ± 0.45 a	8.82 ± 1.20 b	7.50 ± 0.98 b	0.19 ± 0.02 a	0.14 ± 0.03 a	0.07 ± 0.01 c
2	10.47 ± 0.35 a	7.79 ± 1.48 b	7.32 ± 0.46 b	2.27 ± 0.18 a	0.91 ± 0.30 b	1.05 ± 0.45 b
3	9.60 ± 0.44 a	7.01 ± 0.38 b	6.53 ± 0.34 b	2.10 ± 0.09 a	1.04 ± 0.06 b	0.87 ± 0.11 b
4	17.52 ± 1.47 a	14.10 ± 1.48 b	14.27 ± 1.22 b	23.76 ± 1.80 a	14.23 ± 1.50 b	13.93 ± 1.72 b
5	15.29 ± 1.89 a	12.97 ± 0.70 a	12.90 ± 0.75 a	23.61 ± 2.85 a	14.28 ± 0.59 b	13.93 ± 1.20 b
6	15.55 ± 1.45 a	13.95 ± 0.59 a	13.68 ± 1.18 a	23.52 ± 2.01 a	16.93 ± 1.21 b	15.26 ± 2.68 b
7	29.99 ± 1.42 a	22.34 ± 2.86 b	20.99 ± 0.84 b	137.77 ± 12.67 a	79.74 ± 7.55 b	70.48 ± 5.46 b
8	26.89 ± 3.44 a	19.88 ± 2.29 b	19.46 ± 1.60 b	124.26 ± 17.69 a	62.20 ± 4.04 b	53.47 ± 8.35 b
9	25.28 ± 1.95 a	18.95 ± 2.44 b	19.00 ± 1.47 b	118.30 ± 12.10 a	69.19 ± 9.96 b	57.27 ± 2.60 b

Runs 1–9 are the same as that in Table 2. Values are mean ± SD. Means within a row followed by the same letter are not significantly different ($P > 0.05$).

Table 5 TN concentrations and loads by the treatment of LSAA or PAM

Run	Concentration ($\times 10^{-2}$ g/(L·min·m ²))			Loads (mg/(min·m ²))		
	Control	LSAA	PAM	Control	LSAA	PAM
1	33.26 ± 0.03 a	32.44 ± 0.47 b	32.91 ± 0.28 b	0.01 ± 0.001 a	0.005 ± 0.001 a	0.003 ± 0.001 a
2	31.38 ± 0.87 a	31.14 ± 0.70 a	31.27 ± 0.60 a	0.07 ± 0.001 a	0.04 ± 0.01 b	0.05 ± 0.02 a
3	31.32 ± 0.28 a	31.66 ± 0.03 a	31.62 ± 0.11 a	0.07 ± 0.001 a	0.05 ± 0.001 b	0.04 ± 0.003 b
4	70.02 ± 0.70 a	68.01 ± 1.12 a	69.33 ± 0.74 a	0.95 ± 0.05 a	0.69 ± 0.03 b	0.68 ± 0.02 b
5	69.84 ± 1.14 a	64.32 ± 0.49 b	69.01 ± 0.16 a	1.08 ± 0.03 a	0.71 ± 0.04 b	0.75 ± 0.05 b
6	69.07 ± 0.34 a	63.40 ± 0.67 b	68.11 ± 0.96 a	1.05 ± 0.03 a	0.77 ± 0.05 b	0.76 ± 0.08 b
7	100.21 ± 0.48 a	94.01 ± 0.92 b	100.63 ± 0.16 a	4.60 ± 0.24 a	3.37 ± 0.09 b	3.38 ± 0.24 b
8	110.89 ± 2.53 a	103.88 ± 0.51 b	102.29 ± 2.03 b	5.12 ± 0.05 a	3.27 ± 0.30 b	2.90 ± 0.19 b
9	109.06 ± 1.09 a	101.09 ± 0.56 b	100.07 ± 1.87 b	5.10 ± 0.18 a	3.69 ± 0.80 b	3.04 ± 0.16 c

Runs 1–9 are the same as that in Table 2. Values are mean ± SD. Means within a row followed by the same letter are not significantly different ($P > 0.05$).

Table 6 TP concentration and loads by the treatment of LSAA or PAM

Run	Concentration ($\times 10^{-2}$ mg/(L·min·m ²))			Loads ($\times 10^{-2}$ mg/(min·m ²))		
	Control	LSAA	PAM	Control	LSAA	PAM
1	1.72 ± 0.03 a	8.82 ± 1.20 b	7.50 ± 0.98 b	0.03 ± 0.002 a	0.02 ± 0.003 a	0.02 ± 0.002 b
2	10.47 ± 0.35 a	7.79 ± 1.48 b	7.32 ± 0.46 b	0.36 ± 0.06 a	0.17 ± 0.03 b	0.19 ± 0.08 b
3	9.60 ± 0.44 a	7.01 ± 0.38 b	6.53 ± 0.34 b	0.26 ± 0.02 a	0.18 ± 0.01 b	0.16 ± 0.02 b
4	17.52 ± 1.47 a	14.10 ± 1.48 b	14.27 ± 1.22 b	5.27 ± 0.28 a	3.45 ± 0.12 b	3.37 ± 0.27 b
5	15.29 ± 1.89 a	12.97 ± 0.70 a	12.90 ± 0.75 a	4.96 ± 0.36 a	3.86 ± 0.55 b	3.14 ± 0.16 c
6	15.55 ± 1.45 a	13.95 ± 0.59 a	13.68 ± 1.18 a	5.01 ± 0.24 a	3.41 ± 0.28 b	3.06 ± 0.34 b
7	29.99 ± 1.42 a	22.34 ± 2.86 b	20.99 ± 0.84 b	33.66 ± 2.84 a	24.15 ± 0.71 b	23.10 ± 1.89 b
8	26.89 ± 3.44 a	19.88 ± 2.29 b	19.46 ± 1.60 b	32.71 ± 1.96 a	21.70 ± 1.76 b	19.74 ± 2.90 b
9	25.28 ± 1.95 a	18.95 ± 2.44 b	19.00 ± 1.47 b	32.53 ± 2.32 a	23.73 ± 1.86 b	20.33 ± 1.01 c

Runs 1–9 are the same as that in Table 2. Means within a row followed by the same letter are not significantly different ($P > 0.05$).

Table 7 CO₂ emissions by the treatments

Time (d)	CO ₂ concentration (μg/(g·d))			
	Control	LSAA 2 kg/hm ²	LSAA 4 kg/hm ²	LSAA 6 kg/hm ²
2	4.38 ± 0.28 a	4.30 ± 0.20 a	4.29 ± 0.25 a	4.32 ± 0.08 a
4	16.42 ± 0.63 b	16.21 ± 0.10 b	16.57 ± 0.06 a	16.35 ± 0.20 a
8	11.92 ± 0.64 a	11.37 ± 0.06 a	11.59 ± 0.47 a	9.61 ± 1.07 b
12	11.50 ± 0.05 a	11.21 ± 0.14 b	10.63 ± 0.23 c	9.64 ± 1.03 d
15	10.45 ± 0.21 c	10.31 ± 0.48 c	11.53 ± 0.10 a	10.75 ± 0.35 b

Values are mean ± SD. Means within a row followed by the same letter are not significantly different ($P > 0.05$).

Table 8 Urease activity of different treatments

Time (d)	Urease activity (μg/(g·d))			
	Control	LSAA 2 kg/hm ²	LSAA 4 kg/hm ²	LSAA 6 kg/hm ²
2	28.09 ± 0.04 c	28.26 ± 0.03 b	28.45 ± 0.06 b	28.43 ± 0.02 a
4	28.09 ± 0.04 b	28.27 ± 0.04 a	28.06 ± 0.05 b	28.25 ± 0.04 a
8	27.82 ± 0.03 a	27.82 ± 0.03 a	27.85 ± 0.03 a	27.83 ± 0.07 a
12	27.97 ± 0.01 a	27.94 ± 0.04 a	28.01 ± 0.06 a	27.97 ± 0.02 a
15	27.96 ± 0.02 b	27.61 ± 0.06 c	27.93 ± 0.06 b	28.10 ± 0.02 a

Values are mean ± SD. Means within a row followed by the same letter are not significantly different ($P > 0.05$).

possible harm from LSAA to the soil biology.

3 Conclusions

A novel lignin copolymer LSAA was synthesized to apply on controlling non-point pollution resulted from surface runoff. FT-IR showed it owned some new hydrophilic polar function groups such as $-\text{COO}^-$ and $-\text{CONH}$, which might enhance the interaction between the copolymer and soil particles. The research on its environment safety indicated that LSAA is not harmful to the soil microbe.

The results of field experiment indicated that LSAA significantly affected the output of runoff, TSS, COD_{Cr}, TN and TP. The runoff quantity was decreased by 16.67%–47.00% and the loads of TSS, COD, TN, and TP were reduced by 17.78%–62.14%, 26.32%–59.91%, 26.67%–42.86%, and 22.18%–52.78%, respectively. Meanwhile, the comparison of LSAA and PAM showed that the differences between these two products were small on controlling pollutants output. At the aspect of economy, the cost of LSAA is much lower than that of PAM as one major material of LSAA is lignin, which is of great amount and low cost. As calculation, one ton of LSAA costs only 12,550 RMB, which reduces 27% the cost of PAM.

LSAA is a new product. Its performance and environment safety were tested, but its reaction mechanism with soil is still not clear. Besides, the product practical performance is greatly influenced by soil type and vegetation. Therefore, more studies are demanded to support the application of LSAA.

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