Carbohydrate Polymers 81 (2010) 441–447

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Effect of graft copolymerization of fir sawdust lignocellulose with N-vinylpyrrolidone on adsorption capacity to tea catechins

J.H. Ye[a], J.J. Dong[a], J.L. Lu[b], X.Q. Zheng[a], J. Jin[a], H. Chen[a], Y.R. Liang[a,*]

[a] Zhejiang University, Tea Research Institute, 268 Kaixuan Road, Hangzhou 310029, China
[b] Key Laboratory of Horticultural Plants Growth, Development and Biotechnology, Agricultural Ministry of China, Hangzhou 310029, China

ARTICLE INFO

Article history:
Received 30 December 2009
Received in revised form 16 February 2010
Accepted 25 February 2010
Available online 7 March 2010

Keywords:
Cunninghamia lanceolata
Graft copolymerization
Lignocellulose
N-vinylpyrrolidone
Catechins

ABSTRACT

Fir sawdust lignocellulose (FSL) adsorbent was copolymerized with N-vinylpyrrolidone (NVP) in four solvent systems so as to improve its adsorption capacity to tea catechins. It showed that the improvement of adsorption capacity to total catechins was influenced by the reaction solvent, ratio of azodiisobutyronitrile (AIBN) to NVP, ratio of NVP to FSL, reaction temperature and time. The optimum graft copolymerization conditions were: acetonitrile as reaction solvent, AIBN/NVP 0.04, NVP/FSL 0.2 at 70 °C for 6 h. Scanning electron microscopy revealed that the grafted-on NVP was deposited on the FSL surface and in the intercellular regions of the grafted FSL. Fourier transforms infrared spectrum showed that the FSL absorption band at 1634.87 cm^{-1} induced by –C=O was shifted to around 1660 cm^{-1} and the absorption band was greatly strengthened after NVP grafting.

1. Introduction

Lignocellulose prepared from unwanted woody materials was confirmed to be used as an inexpensive useful adsorbent to isolate bioactive components from plants or remove heavy metal ions from aqueous solutions (Sakanaka, 2003; Shukla, Yu, Dorris, & Shukla, 2005; Shukla, Zhang, Dubey, Margrave, & Shukla, 2002; Yoshita, Lu, Ye, & Liang, 2009). The lignocellulose has abundant hydroxyl and carbonyl groups which are expected to interact with polyphenols or heavy metal ions by hydrogen bonding or complexation (Adler, 1977; Chakar & Ragauskas, 2004; Dizhbite et al., 1999). However, the effectiveness of these functional groups is suppressed by intermolecular forces and crystallinities of the wood cellulose fibers (Tiemann, Gardea-Torresdey, Gamez, Dokken, & Sias, 1999), resulting in a low adsorption capacity to polyphenols or heavy metal ions on lignocellulose, compared with artificial synthetic polymers.

Graft copolymerization method was used to appending new functional groups to natural polymeric adsorbents so as to increase their adsorption capacities or improve the mechanical properties (Farag & Al-Afaleq, 2002; Mondal, Uraki, Ubukata, & Itoyama, 2008; Sciban, Klasnja, & Skrbic, 2006). Lignocellulose has multiplicate functional groups which are suitable for graft modification (Chauhan, Chauhan, Kumar, & Kumari, 2008; Ouajai, Hodzic, & Shanks, 2004). Methyl acrylate was grafted onto rubber wood fiber (Abu-Ilaiwi et al., 2004), and methacrylic acid was applied to modify the biodegradable lignocellulose, resulting in the improvement of mechanical and thermal properties of the adsorbent (Khan, 2004). Acrylamide was grafted onto cotton cellulose and sisal lignocellulose, and its grafting efficiency on cotton cellulose was higher than that on sisal lignocellulose (Gangopadhyay & Ghosh, 1999).

Polyamide and protein with acylamido group have strong affinities to polyphenols through hydrogen bonding or complexation. Polyvinylpyrrolidone (PVP) is an effective adsorbent for polyphenols by virtue of the action of acylamido groups which play the same role as those in polyamide and protein (Haaf, Sanner, & Straub, 1985). However, the high hydrophile and gelation of PVP obstructed a large-scale separation and purification of polyphenols. N-vinylpyrrolidone (NVP), the monomer of PVP with acylamido and vinyl groups, is a promising reagent for modification of lignocellulose owing to its non-toxicity, hydrophilicity and high tendency toward complexation (Chopabaeva & Ergozhin, 2008).

In this paper, we investigated the graft copolymerization of NVP onto fir sawdust lignocellulose (FSL) initiated by azodiisobutyronitrile (AIBN) in different solvent-borne systems, and the changes in adsorbilities of the grafted adsorbents were investigated by testing its adsorption to tea catechins from tea solution. The effect of reaction conditions including kinds of solvents, initiator and monomer concentrations, temperature and reaction time on the adsorption capacity were studied. The changes in lignocellulose structure and spectrum character after NVP graft copolymerization were evaluated by scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR).

---

* Corresponding author. Tel.: +86 571 86971260; fax: +86 571 86971704.
E-mail address: yrliang@zju.edu.cn (Y.R. Liang).

0144-8617/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2010.02.045

2. Experimental

2.1. Materials

The fir (*Cunninghamia lanceolata*) sawdust was provided by Hangzhou Lumber Mill (Hangzhou, China). N-vinylpyrrolidone (NVP) and azodiisobutyronitrile (AIBN) were Sigma products (Sigma–Aldrich, St. Louis, USA). The AIBN was purified twice, each time by precipitation using ethanol and drying in a vacuum oven at room temperature for 48 h. Green tea extract was supplied by the Orient Tea Development Co. Ltd. (Hangzhou, China). Chemical purity grade ethanol was purchased from Sinopharm Chemical Reagent Co. Ltd. (Beijing, China). HPLC reference compounds including (−)epigallocatechin gallate (EGCg), (−)epigallocatechin (EGC), (−)epicatechin gallate (ECg), (−)epicatechin (EC), (+)gallocatechin gallate (GCg), (+)gallocatechin (GC), (+)catechin gallate (Cg), (+)catechin (C) were supplied by National Institute of Japan (Kagoshima, Japan), and caffeine was a Sigma product (Sigma–Aldrich, St. Louis, USA). The other chemical reagents used were of HPLC grade (Jinmei Biotech Corporation, Tianjin, China). The water used in the experiments was de-ionized water.

2.2. Preparation of lignocellulose

Lignocellulose preparation was carried out according to the modified method as demonstrated (Sakanaka, 2003; Ye et al., 2009). The fir sawdust was dried at 105 °C for 4 h and then ground using a EUPA TSK-927S grinder (Cankun Co. Ltd., Shanghai, China). Screened particles of size 0.25–0.30 mm, were then drenched in 2 volumes of 0.1N NaOH for 72 h at room temperature. The NaOH solution was drained and the plant material was washed with water. The NaOH-treated material was drenched in 2 volumes of 0.1N HCl overnight and then washed with water to pH 7, and finally suspended in 2 volumes of 95% ethanol overnight at room temperature and washed again with water (Ye et al., 2009). The obtained fir sawdust lignocelluloses (FSL) was dried under ambient conditions and used as adsorbent in the tests.

2.3. Graft copolymerization

The FSL (10.0 g) was placed in a 250-mL 3-necked round-bottomed flask fitted with condenser, thermometer and stirrer. The predetermined amounts of monomer NVP, initiator AIBN and 50 mL solvent were added into the flask. The assembly was purged with nitrogen gas for 30 min to remove oxygen, and then placed in a thermostat water bath preset at a designed temperature (50–70 °C) for a designed reaction time (2–8 h). The grafted samples were refluxed in a soxhlet apparatus for 24 h using ethanol as a solvent so as to remove the residue monomer and homopolymer. The graft copolymer was then washed with distilled water and dried in an oven at 40 °C for 24 h.

2.4. Scanning electron microscopy (SEM)

SEM studies of the FSL and NVP-grafted samples were performed using a XL-30-ESEM (Philips, Amsterdam, Holand) according to the manufacturer's manual.

2.5. Fourier transforms infrared (FTIR) spectrum

To analyze the chemical and/or physical interactions after grafting, a Nicolet AVATAR 370 FTIR Spectrometer (Thermo Fisher, Massachusetts, USA) was used to determine the FTIR spectrum of FSLs before and after grafting in KBr pellets in the wave length ranging from 400 to 4000 cm^{-1} according to method described by Yang, Li, He, Ren, and Wang (2009).

2.6. Test of adsorption capacity

Five g of the grafted adsorbents was placed in a 100-mL conical flask containing 50 mL of tea extract solution (5 $g\,L^{-1}$). The flasks were shaken at 150 rpm and 25 °C for 6 h in a H2S-H water bath shaker (Donglian Electronic Technology Co. Ltd., Harbin, China) and then the supernatants were sampled for HPLC. The adsorption capacity was calculated by the following Eq. (1):

$$q = \frac{V(C_0 - C)}{G} \qquad (1)$$

where q is the adsorption capacity of the adsorbent ($mg\,g^{-1}$) at equilibrium, C_0 and C are the initial and final solute concentrations of the solution ($mg\,mL^{-1}$), respectively. V is the solution volume (mL) and G is the weight of the adsorbent used (g).

2.7. HPLC analysis of catechins and caffeine

Concentrations of catechins and caffeine were analyzed by modified method described in previous paper (Liang et al., 2007). The HPLC conditions were: injection volume 10 μL, phenomenex C_{18} column (4.6 mm × 150 mm), column temperature 28 °C, mobile phase A = acetonitrile/acetic acid/water (6:1:193, v), mobile phase B = acetonitrile/acetic acid/water (60:1:139, v), linear gradient elution from 70% A/30% B (v) to 15% A/85% B (v) during the early 33 min and then remained 15% A/85% B (v) till 38 min, flow rate 1 $mL\,min^{-1}$. The eluate was monitored by a Shimadzu SPD ultraviolet detector at 280 nm.

2.8. Data analysis

Tests in the present paper were carried out in triplicate and the mean values of the triplicate tests are presented.

3. Results and discussion

3.1. Effect of reaction solvents on adsorption capacities of the grafted FSL

Four organic solvents were used as reaction solutions in the graft copolymerization. The adsorption capacities of the NVP-grafted FSLs to the catechins increased, compared to the ungrafted control (Table 1). The reaction solvents had significant influence on the adsorption capacity to total catechins. Among the NVP-grafted FSLs, the FSL grafted in acetonitrile had the highest adsorption capacity to total catechins, with a mean value 101.40 $mg\,g^{-1}$ or 36.98% higher than that of the ungrafted FSL, and that grafted in chloroform had the lowest adsorption capacity, with those grafted in acetone and xylene in between (Table 1). Among the adsorbed catechins, the concentration of both EGCG and ECG was the highest. The total concentration of EGCG and ECG was more than 78% of total catechins. However, the adsorption capacity to caffeine for the NVP-grafted FSLs decreased, compared with the ungrafted FSL control. This study suggests that the adsorption capacity and adsorption selectivity of the FSL adsorbents were improved after graft copolymerization. Based on the adsorption capacities shown in Table 1, acetonitrile and acetone were selected as reaction solvents in the subsequent tests.

3.2. Effect of AIBN/NVP ratio on adsorption capacity of NVP-grafted FSLs

The adsorption capacity of the NVP-grafted FSLs copolymerized in acetonitrile and in acetone increased with the increase in the AIBN/NVP ratio up to 0.04 and 0.06 respectively and then remained

Table 1
The effect of reaction solvents on adsorption capacity of NVP-grafted FSL to tea catechins (mg g^{-1})[a].

Reaction solvent[b]	GC	EGC	C	EC	EGCG	GCG	ECG	CG	Total catechins[c]	Caffeine
Acetonitrile	2.030 ± 0.059	15.096 ± 0.595	0.381 ± 0.150	3.883 ± 0.046	62.310 ± 0.304	2.401 ± 0.007	14.944 ± 0.039	0.356 ± 0.001	101.400 ± 1.103 (136.98%)	4.242 ± 0.112
Acetone	0.868 ± 0.180	10.070 ± 0.422	0.400 ± 0.009	2.688 ± 0.099	56.216 ± 0.236	2.292 ± 0.007	14.465 ± 0.037	0.359 ± 0.002	87.357 ± 0.878 (118.01%)	4.334 ± 0.156
Xylene	0.952 ± 0.008	9.748 ± 0.055	0.381 ± 0.002	2.539 ± 0.015	54.239 ± 0.121	2.237 ± 0.003	14.141 ± 0.019	0.362 ± 0.013	84.599 ± 0.235 (114.28%)	4.614 ± 0.023
Chloroform	0.755 ± 0.216	9.068 ± 0.433	0.367 ± 0.009	2.564 ± 0.024	53.770 ± 0.098	2.230 ± 0.002	14.065 ± 0.013	0.374 ± 0.002	83.194 ± 0.796 (112.38%)	4.668 ± 0.030
Ungrafted	0.972 ± 0.011	8.264 ± 0.035	0.304 ± 0.001	2.150 ± 0.110	46.904 ± 0.119	2.079 ± 0.004	13.027 ± 0.018	0.327 ± 0.001	74.028 ± 0.298 (100%)	4.781 ± 0.026

[a] 0.25 g of tea extract dissolved in 50 mL of water was shaken with, 5.0 g adsorbent at 150 rpm and 25 °C for 6 h; the data were expressed as mean ± standard deviation ($n = 3$).
[b] *Reaction conditions*: FSL 10 g, NVP 2 mL, reaction solvent = 50 mL, AIBN/NVP = 1/10, 70 °C, 6 h.
[c] Data in the brackets were the percentages compared to the ungrafted control.

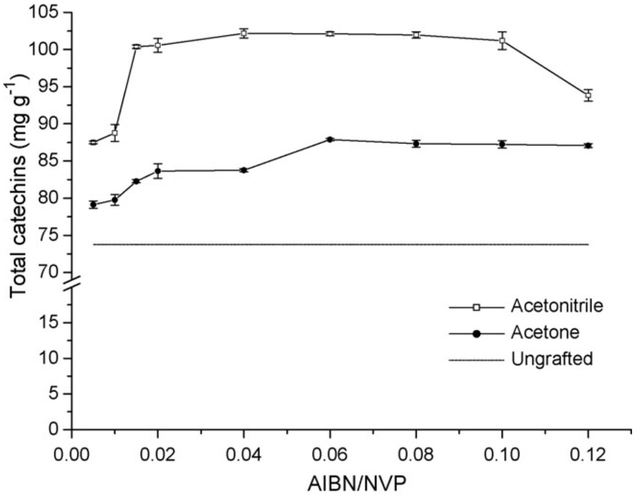

Fig. 1. Effect of the AIBN/NVP ratio on the adsorption capacity to total catechins. *Reaction conditions*: FSL 10 g, NVP 2 mL, solvent 50 mL, at 70 °C for 6 h.

stable (Fig. 1). However, the NVP-grafted FSL copolymerized in acetonitrile decreased markedly as the AIBN/NVP ratio was above 0.1. The AIBN was used as an initiator to generate free radical [AIBN•] in the copolymerization reaction. Fig. 1 shows that the initiation effect of AIBN was influenced by reaction solvents. The optimum ratio of AIBN/NVP was 0.04 for acetonitrile, and that for acetone was 0.06.

Many works have been focused on the reaction mechanism of graft copolymerization of natural polymer recently (Mondal, Uraki, Ubukata, & Itoyama, 2008; Pourjavadi, Harzandi, & Hosseinzadeh, 2004). Lignocellulose is mainly composed of lignin, cellulose and hemicelluloses (Sjöström, 1981). Major part of hemicelluloses were hydrolyzed or removed in the process of lignocellulose preparation, and most of the remaining active groups for graft copolymerization were located on lignin and cellulose. Phenolic hydroxyl groups of lignin and hydroxyl groups of cellulose might be the important active sites for polymerization reaction, and lignin was considered to be more sensitive to polymerization than cellulose (Huang, Zhao, Zheng, He, & Gao, 1992). The weak homolytic bonding of AIBN is broken under heating conditions, resulting in generation of free radical [AIBN•]. The free radical extracts the hydrogen from the phenolic hydroxyl group, which induces an active reaction center on the substrate. That is why the AIBN can initiate graft polymerization of NVP. The mechanism of grafting NVP onto the FSL initiated by AIBN might follow three steps, i.e., initiation, chain transfer and termination as shown in Fig. 2.

When the initiator AIBN concentration increased, the level of free radicals [AIBN•] increased, which initiated the formation of [FSL•]. The [FSL•] interacted with NVP, resulting in the formation of [∼FSL–NVP•]. In this case, the grafting degree is increased. The functional groups of NVP grafted on the FSL contributed to the increase in adsorption capacity to catechins. However, the excessive [AIBN•] and [FSL•] will aggravate chain termination, which will lead to abundant homopolymerization and depression in the grafting efficiency of NVP. That explains why the adsorbility of the FSLs grafted at higher levels of AIBN was not increased (Fig. 1).

3.3. Effect of NVP/FSL ratio on the adsorption capacity of grafted FSL

The influence of NVP/FSL ratio on the adsorption capacity to total catechins depended on the reaction system. The adsorption capacity of NVP-grafted FSL copolymerized in acetonitrile increased from

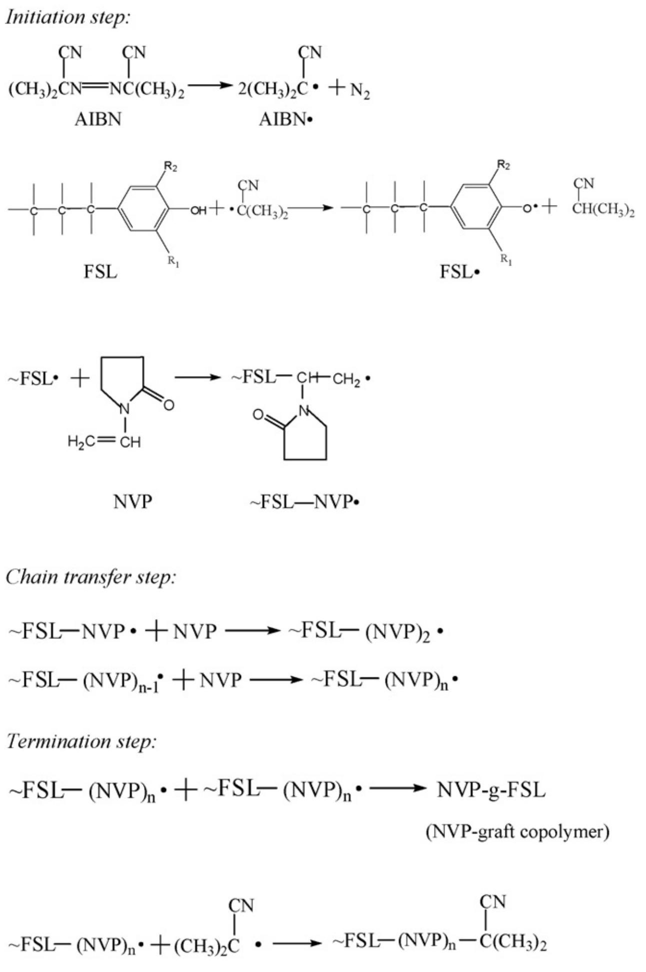

Fig. 2. A proposed mechanism for synthesis of NVP-grafted FSLs.

87.056 to 102.592 mg g^{-1} as the ratio of NVP/FSL increased from 0.1 to 0.2, being 39% higher than the ungrafted control, and then remained at a level around 103 mg g^{-1} even though the ratio of NVP/FSL was further increased. When the graft copolymerization was carried out in acetone, the adsorption capacity increased continuously with increase in the NVP/FSL ration up to 0.8 (Fig. 3). However, there was no significant difference in the highest adsorption levels between the acetonitile system (NVP/FSL = 0.2) and acetone system (NVP/FSL = 0.8). This suggests that grafting efficiency of NVP in acetonitrile system is higher than that in acetone system.

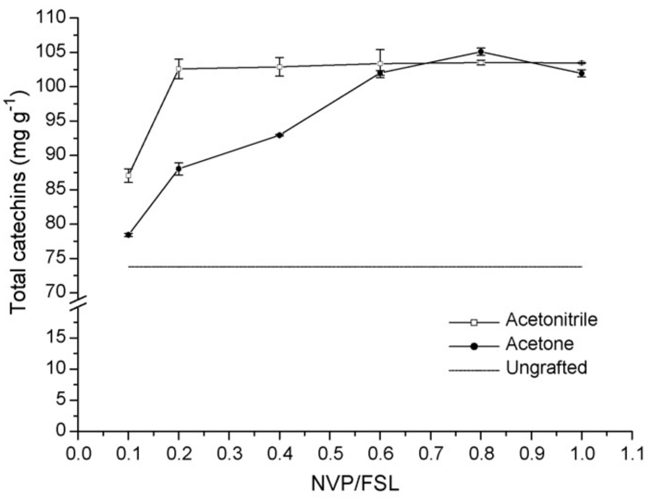

Fig. 3. The effect of NVP/FSL ratio on the adsorption capacity to total catechins. *Reaction conditions*: FSL 10 g, NVP 1–10 mL, solvent 50 mL, AIBN/NVP 6/100, at 70 °C for 6 h.

The carbonyl of the lignocelluose and acylamide of the NVP are functional groups which interact with hydroxyl groups of catechins. The polarity of carbonyl in the acylamido is stronger than that of lignocellulose because of the electron attraction effect of nitrogen. Therefore the intensity of hydrogen bonding between acylamide of the NVP and hydroxyl groups of tea catechins would be stronger than the action between carbonyl of FSL and hydroxyl groups of catechins. This resulted in the improvement of adsorption capacities of NVP-grafted FSL. With an increase of monomer concentration, a large number of monomer free radicals accumulate close to the backbone and give rise to graft copolymerization. However, the primary radicals attacked the monomer instead of the FSL at higher monomer concentration, resulting in a drastic homopolymerization reaction and low graft yield (Hsu & Pan, 2007; Kaith, Jindal, Jana, & Maiti, 2009). Therefore the adsorption capacity of total catechins hardly increased when the ratio of NVP/FSL exceeded 0.2 as shown in Fig. 3.

3.4. *Effect of graft copolymerization temperature and time on the adsorption capacity of grafted FSL*

Graft copolymerization of NVP onto FSL was carried at temperature ranging from 50 to 70 °C. The results showed that the adsorption capacities to tea catechins for FSLs grafted in acetonitrile and acetone increased with the increase in the reaction temperature. The maximum adsorption capacity was obtained at 70 °C for both acetonitrile and acetone (Table 2). Since AIBN is a thermal initiator which was drastically dissociated above 80 °C, it is proposed that the graft copolymerization be carried out at 70 °C in order to gain a high grafting degree.

It was observed that the adsorption capacities to total catechins for FSLs grafted in both acetonitrile and acetone increased over time (Table 3). However, there was no significant difference between 6 and 8 h. From the data, it is recommended that graft copolymerization time should not be less than 6 h.

3.5. *Scanning electron microscopy (SEM)*

SEM micrographs of ungrafted FSL and NVP-grafted FSLs are shown in Fig. 4. It was obvious that there were crystals and cracks on the surface of ungrafted FSL (Fig. 4a). The difference between the surface morphology of grafted FSLs and that of ungrafted fiber could be observed visually. The surface morphology of NVP-grafted FSL changed markedly and it looked uniform and smooth because the grafted-on NVP was deposited on the FSL surface as well as in the intercellular regions of the grafted FSLs (Fig. 4b and c). However, difference in grafting efficiency between NVP-grafted FSL copolymerized in acetonitrile and that in acetone was obvious. The FSL copolymerized in acetonitrile had more grafted-on NVP than that copolymerized in acetone and crystallinities were partially observed on surface of NVP-grafted FSL copolymerized in acetone (Fig. 4b and c). The crystallinities of the wood cellulose fibers suppress the action of active groups and adsorption capacity (Tiemann et al., 1999). This explains why NVP-grafted FSL copolymerized in acetone had lower adsorption capacity than that copolymerized in acetonitrile (Fig. 1).

3.6. *FTIR spectra*

Absorption bands related to bonds of O–H, C–O–C, C–H, and C–C were identified in the FTIR spectrum of ungrafted FSL (Fig. 5a).

Table 2

The influence of copolymerization temperature on the adsorption capacity to total catechins (mg g^{-1}).[a].

	Temp.[b]	GC	EGC	C	EC	EGCG	GCG	ECG	CG	Total catechins[c]	Caffeine
Acetonitrile	50 °C	1.734 ± 0.061	11.191 ± 0.209	0.350 ± 0.006	3.239 ± 0.045	59.130 ± 0.145	2.307 ± 0.011	14.388 ± 0.041	0.350 ± 0.003	92.689 ± 0.316 (127.50%)	4.035 ± 0.076
	60 °C	1.873 ± 0.064	12.126 ± 0.080	0.370 ± 0.002	3.450 ± 0.014	61.368 ± 0.237	2.363 ± 0.002	14.766 ± 0.025	0.356 ± 0.003	96.672 ± 0.241 (132.98%)	3.906 ± 0.049
	70 °C	1.868 ± 0.032	14.491 ± 0.099	0.385 ± 0.009	3.777 ± 0.014	62.721 ± 0.045	2.409 ± 0.006	15.709 ± 0.033	0.371 ± 0.001	101.730 ± 0.127 (139.93%)	3.994 ± 0.019
Acetone	50 °C	1.691 ± 0.062	10.697 ± 0.095	0.360 ± 0.002	3.131 ± 0.012	58.930 ± 0.025	2.295 ± 0.001	14.338 ± 0.006	0.359 ± 0.000	91.802 ± 0.154 (126.28%)	4.009 ± 0.030
	60 °C	1.900 ± 0.064	12.163 ± 0.071	0.390 ± 0.002	3.472 ± 0.004	61.426 ± 0.184	2.364 ± 0.001	14.774 ± 0.016	0.392 ± 0.004	96.879 ± 0.295 (133.26%)	3.928 ± 0.030
	70 °C	1.966 ± 0.061	14.931 ± 0.126	0.419 ± 0.010	3.641 ± 0.031	63.807 ± 0.265	2.474 ± 0.003	15.885 ± 0.017	0.383 ± 0.002	103.505 ± 0.452 (142.38%)	3.974 ± 0.031
Ungrafted		0.808 ± 0.057	8.366 ± 0.386	0.298 ± 0.013	2.459 ± 0.033	46.367 ± 0.082	1.981 ± 0.002	12.076 ± 0.093	0.345 ± 0.004	72.699 ± 0.450 (100%)	4.726 ± 0.048

[a] 0.25 g of tea extract dissolved in 50 mL of water was shaken with, 5.0 g adsorbent at 150 rpm and 25 °C for 6 h; the data were expressed as mean ± standard deviation ($n = 3$).

[b] *Reaction conditions*: FSL 10 g, NVP 8 mL, reaction solvent 50 mL, AIBN/NVP 6/100, 50–70 °C, 6 h.

[c] Data in the brackets were the percentages compared to the ungrafted control.

Table 3

The influence of copolymerization time on the adsorption capacity to total catechins (mg g^{-1}).[a].

	Time[b]	GC	EGC	C	EC	EGCG	GCG	ECG	CG	Total catechins[c]	Caffeine
Acetonitrile	2 h	1.253 ± 0.058	10.351 ± 0.104	0.376 ± 0.008	2.987 ± 0.022	52.097 ± 0.259	2.138 ± 0.001	13.233 ± 0.019	0.361 ± 0.002	82.796 ± 0.460 (114.04%)	4.205 ± 0.023
	4 h	2.100 ± 0.164	14.259 ± 0.295	0.457 ± 0.007	3.588 ± 0.050	61.941 ± 0.129	2.324 ± 0.005	15.366 ± 0.026	0.367 ± 0.001	100.402 ± 0.635 (138.29%)	4.102 ± 0.069
	6 h	1.940 ± 0.185	14.795 ± 0.148	0.509 ± 0.010	3.616 ± 0.020	62.733 ± 0.125	2.387 ± 0.002	15.342 ± 0.011	0.371 ± 0.001	101.695 ± 0.476 (140.07%)	3.966 ± 0.010
	8 h	2.065 ± 0.080	15.081 ± 0.124	0.533 ± 0.002	3.663 ± 0.027	63.386 ± 0.049	2.431 ± 0.002	15.380 ± 0.007	0.387 ± 0.001	102.925 ± 0.176 (141.77%)	3.849 ± 0.036
Acetone	2 h	1.727 ± 0.195	12.456 ± 0.278	0.386 ± 0.013	3.563 ± 0.044	61.798 ± 0.195	2.366 ± 0.003	14.971 ± 0.020	0.365 ± 0.001	97.633 ± 0.747 (134.48%)	4.276 ± 0.032
	4 h	1.985 ± 0.067	14.673 ± 0.036	0.455 ± 0.001	3.641 ± 0.007	62.728 ± 0.035	2.443 ± 0.001	15.468 ± 0.007	0.374 ± 0.001	101.769 ± 0.145 (140.17%)	4.109 ± 0.013
	6 h	1.921 ± 0.011	15.184 ± 0.074	0.489 ± 0.002	3.689 ± 0.018	63.890 ± 0.063	2.457 ± 0.002	15.537 ± 0.010	0.384 ± 0.001	103.552 ± 0.172 (142.63%)	4.001 ± 0.017
	8 h	1.978 ± 0.025	15.453 ± 0.272	0.601 ± 0.006	3.759 ± 0.062	64.380 ± 0.089	2.473 ± 0.003	15.627 ± 0.016	0.410 ± 0.001	104.681 ± 0.418 (144.19%)	3.978 ± 0.014
Ungrafted		0.722 ± 0.011	8.530 ± 0.244	0.299 ± 0.010	2.456 ± 0.020	45.994 ± 0.026	2.047 ± 0.005	12.209 ± 0.072	0.345 ± 0.002	72.602 ± 0.354 (100%)	4.743 ± 0.051

[a] 0.25 g of tea extract dissolved in 50 mL of water was shaken with, 5.0 g adsorbent at 150 rpm and 25 °C for 6 h; the data were expressed as mean ± standard deviation ($n = 3$).

[b] *Reaction conditions*: FSL 10 g, NVP 8 mL, solvent 50 mL, AIBN/NVP 6/100, 70 °C, 2–6 h.

[c] Data in the brackets were the percentages compared to the ungrafted control.

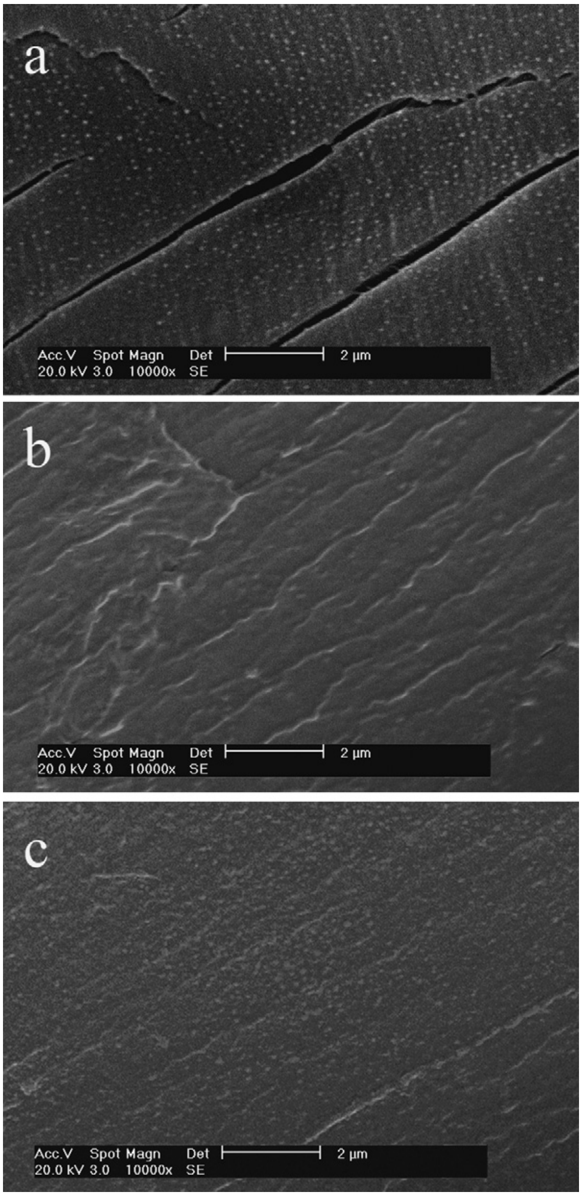

Fig. 4. Scanning electron micrographs of FSLs before and after grafting. *Reaction conditions*: FSL 10 g, NVP 2 mL, reaction solvent 50 mL, AIBN/NVP 4/100, at 70 °C for 6 h: (a) before grafting; (b) grafted in acetonitrile; (c) grafted in acetone.

The broad absorption band at 3417.98 cm^{-1} was attributed to the hydrogen bonding between molecules via –OH groups. The absorption band at 2900.95 cm^{-1} was the stretching vibration of C–H, the band at 1427.40 cm^{-1} was due to the scissoring vibration of –CH$_2$– and that at 1372.41 cm^{-1} the in-plane rocking and bending vibration of –CH$_3$. Bands at 1266.33 and 1058.89 cm^{-1} were assigned to the Ar–O and R–O stretching in lignin. The absorption band at 1634.87 cm^{-1} was related to the functional group carbonyl (–C═O) in the lignin (Fig. 5a). Acylamido is the characteristic functional group of NVP and it is composed of one nitrogen and one carbonyl. After NVP grafting, the absorption band at 1634.87 cm^{-1} induced by –C═O was blue shift to around 1660 cm^{-1} owing to the electron-attracting effect of nitrogen on NVP acylamido. The band was markedly strengthened in the NVP-grafted FSLs copolymerized in both acetonitrile and acetone (Fig. 5b and c). The blue shifting and strengthening of the absoption band due to –C═O confirmed that NVP was grafted onto FSL.

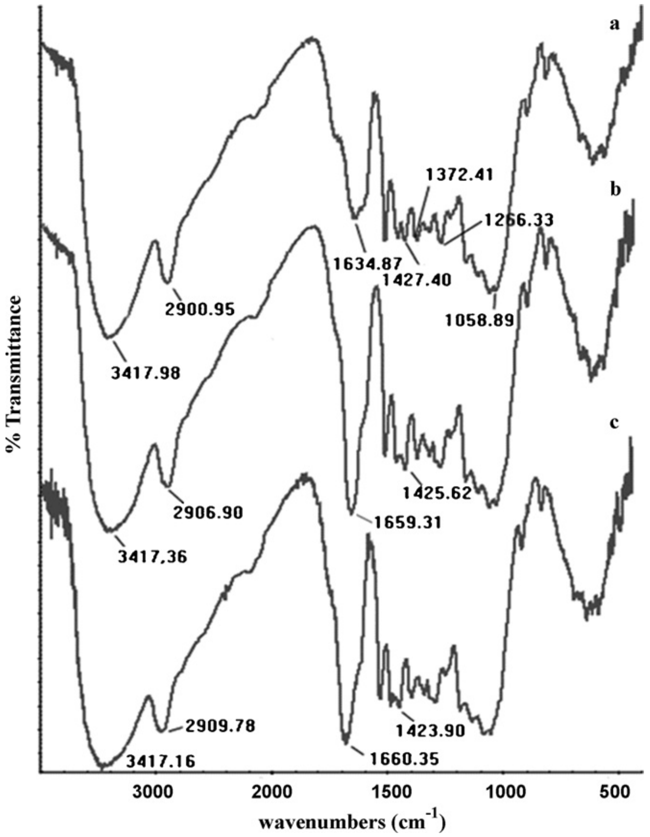

Fig. 5. Effect of grafting on FTIR spectrum of FSLs. *Reaction conditions*: FSL 10 g, NVP 2 mL, solvent 50 mL, AIBN/NVP 4/100, at 70 °C for 6 h: (a) before grafting; (b) grafted in acetonitrile; (c) grafted in acetone.

4. Conclusion

The adsorption capacity of FSL adsorbent to tea catechins was improved by graft copolymerization with N-vinylpyrrolidone (NVP). Acetonitrile was the best reaction solvent among the tested solvents. The optimum copolymerization reaction conditions for acetonitrile were: AIBN/NVP = 0.04, NVP/FSL = 0.2 at 70 °C for 6 h. The SEM micrographs and FTIR spectrum of NVP-grafted FSLs confirmed that NVP was successfully grafted onto FSL. The adsorption capacity to total catechins for the FSL after modification under these condtions was increased by 36–40%. NVP graft copolymerization is considered to be a promising method to improve biopolymer adsorbents for isolating tea catechins.

Acknowledgment

This study was financed by the "Key Technology R&D Program" (project no. 2006B AD27B06) of the Ministry of Science and Technology of China.

References

Abu-Ilaiwi, F. A., Ahmad, M. B., Ibrahim, N. A., Ab Rahman, M. Z., Dahlan, K. Z. M., & Yunnus, W. M. Z. W. (2004). Optimized conditions for the grafting reaction of poly(methyl acrylate) onto rubberwood fiber. *Polymer International*, *53*, 386–391.

Adler, E. (1977). Lignin chemistry—Past, present and future. *Wood Science and Technology*, *11*, 169–218.

Chakar, F. S., & Ragauskas, A. J. (2004). Review of current and future softwood Kraft lignin process chemistry. *Industrial Crops and Products*, *20*, 131–141.

Chauhan, G. S., Chauhan, S., Kumar, S., & Kumari, A. (2008). A study in the adsorption of Fe^{2+} and NO^{3-} on pine needles based hydrogels. *Bioresource Technology*, *99*, 6464–6470.

Chopabaeva, N. N., & Ergozhin, E. E. (2008). Synthesis of graft copolymers of wood and N-vinylpyrrolidone. *Chemistry of Natural Compounds*, *44*, 220–223.

Dizhbite, T., Zakis, G., Kizima, A., Lazareva, E., Rossinskaya, G., Jurkjane, V., et al. (1999). Lignin—A useful bioresource for the production of sorption-active materials. *Bioresource Technology*, *67*, 221–228.

Farag, S., & Al-Afaleq, E. I. (2002). Preparation and characterization of saponified delignified cellulose polyacrylonitrile-graft copolymer. *Carbohydrate Polymers*, *48*, 1–5.

Gangopadhyay, R., & Ghosh, P. (1999). Uncatalyzed photografting of polyacrylamide from functionalized cellulosic and lignocellulosic materials. *Journal of Applied Polymer Science*, *74*, 1623–1634.

Haaf, F., Sanner, A., & Straub, F. (1985). Polymers of N-ninylpyrrolidone: Synthesis, characterization and uses. *Polymer Journal*, *17*, 143–152.

Hsu, S. T., & Pan, T. C. (2007). Adsorption of paraquat using methacrylic acid-modified rice husk. *Bioresource Technology*, *98*, 3617–3621.

Huang, Y. F., Zhao, B. A., Zheng, G. Z., He, S. J., & Gao, J. (1992). Graft copolymerization of methyl methacrylate on stone ground wood using the H_2O_2–Fe^{2+} method. *Journal of Applied Polymer Science*, *45*, 71–77.

Liang, H. L., Liang, Y. R., Dong, J. J., Lu, J. L., Xu, H. R., & Wang, H. (2007). Decaffeination of fresh green tea leaf (*Camellia sinensis*) by hot water treatment. *Food Chemistry*, *101*, 1451–1456.

Kaith, B. S., Jindal, R., Jana, A. K., & Maiti, M. (2009). Characterization and evaluation of methyl methacrylate-acetylated *Saccharum spontaneum* L. graft copolymers prepared under microwave. *Carbohydrate Polymers*, *78*, 987–996.

Khan, F. (2004). Photoinduced graft-copolymer synthesis and characterization of methacrylic acid onto natural biodegradable lignocellulose fiber. *Biomacromolecules*, *5*, 1078–1088.

Mondal, M. I. H., Uraki, Y., Ubukata, M., & Itoyama, K. (2008). Graft polymerization of vinyl monomers onto cotton fibres pretreated with amines. *Cellulose*, *15*, 581–592.

Ouajai, S., Hodzic, A., & Shanks, R. A. (2004). Morphological and grafting modification of natural cellulose fibers. *Journal of Applied Polymer Science*, *94*, 2456–2465.

Pourjavadi, A., Harzandi, A. M., & Hosseinzadeh, H. (2004). Modified carrageenan 3. Synthesis of a novel polysaccharide-based superabsorbent hydrogel via graft copolymerization of acrylic acid onto kappa-carrageenan in air. *European Polymer Journal*, *40*, 1363–1370.

Sakanaka, S. (2003). A novel convenient process to obtain a raw decaffeinated tea polyphenol fraction using a lignocellulose column. *Journal of Agricultural and Food Chemistry*, *51*, 3140–3143.

Sciban, M., Klasnja, M., & Skrbic, B. (2006). Modified softwood sawdust as adsorbent of heavy metal ions from water. *Journal of Hazardous Material*, *136*, 266–271.

Shukla, S. S., Yu, L. J., Dorris, K. L., & Shukla, A. (2005). Removal of nickel from aqueous solutions by sawdust. *Journal of Hazardous Material*, *121*, 243–246.

Shukla, A., Zhang, Y. H., Dubey, P., Margrave, J. L., & Shukla, S. S. (2002). The role of sawdust in the removal of unwanted materials from water. *Journal of Hazardous Material*, *95*, 137–152.

Sjöström, E. (1981). Wood chemistry. In *Fundamentals and applications*. New York: Academic Press Inc., p. 223.

Tiemann, K. J., Gardea-Torresdey, J. L., Gamez, G., Dokken, K., & Sias, S. (1999). Use of X-ray absorption spectroscopy and esterification to investigate Cr(III) and Ni(II) ligands in alfalfa biomass. *Environmental Science & Technology*, *33*, 150–154.

Yang, F., Li, G., He, Y. G., Ren, F. X., & Wang, G. X. (2009). Synthesis, characterization, and applied properties of carboxymethyl cellulose and polyacrylamide graft copolymer. *Carbohydrate Polymers*, *78*, 95–99.

Ye, J. H., Jin, J., Liang, H. L., Lu, J. L., Du, Y. Y., Zheng, X. Q., et al. (2009). Using tea stalk lignocellulose as an adsorbent for separating decaffeinated tea catechins. *Bioresource Technology*, *100*, 622–628.

Yoshita, A., Lu, J. L., Ye, J. H., & Liang, Y. R. (2009). Sorption of lead from aqueous solutions by spent tea leaf. *African Journal of Biotechnology*, *8*, 2212–2217.