

Quaternization and Anion Exchange Capacity of Sponge Gourd (*Luffa cylindrica*)

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ABSTRACT: Gourd (*Luffa cylindrica*) was converted into an anion exchange material through its etherification using 2-chloroethyldiethylamine hydrochloride (CEDA-HCl) followed by crosslinking using epichlorohydrin. The effects of the different etherification reaction parameters (CEDA concentration, NaOH concentration, and temperature) on the extent of modification were followed up by elemental analysis of nitrogen to optimize the reaction. The effect of the etherification on the supramolecular structure was followed by the X-ray diffraction. The ability of the crosslinked dieth-

ylaminoethylated luffa (DEAE-luffa), after its quaternization with methyl iodide, to adsorb sulfate, nitrate, and phosphate anions was tested. The crosslinked DEAE-luffa showed higher affinity toward phosphate anions followed by sulfate and nitrate. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2495–2503, 2006

Key words: *Luffa cylindrica*; etherification; anion exchanger; diethylaminoethyl; quaternized

INTRODUCTION

The use of lignocellulosic materials other than wood has been the object of researchers all over the world because of the necessity for exploring alternative raw materials from renewable resources to reduce the impact on forests and to utilize the huge amounts of agricultural wastes and agro-based fibers. The use of agro-based fibers or agricultural residues in the area of water treatment for removal of different pollutants is of increasing interest because of the renewability of these materials, large availability and low cost, biodegradability, and the ability of their direct modification, i.e., without separation of the main components (cellulose, hemicelluloses, and lignin). Modification reactions including crosslinking and functionalization are commonly applied to enhance adsorption capacity and adsorbent stability of the components present in these lignocellulosic materials. Different anion^{1–6} and cation^{7–13} exchangers have been prepared using different agricultural residues and agro-based fibers, through chemical modification with different functional groups.

Luffa cylindrica is one of these lignocellulosic materials whose potentiality in removing water pollutants has not been explored yet. *L. cylindrica* has a fibrous vascular system in which the fibers are disposed in a

multidirectional array forming a natural mat-like material. Because of its unique natural mat-like material, *L. cylindrica* has been used as a carrier for plant and microbial cells' immobilization,^{14–17} for continuous ethanol production in a column-type bioreactor,^{18–20} lactic acid production,²¹ immobilization of fungal mycelium for decolorization of synthetic dyes,²² and carrier for consortium for biodegradation of some herbicides and fungicides.²³ *Luffa* was also used as carrier for immobilization of some microalgal cells for removal of some heavy metal ions.^{22,24–26} In the area of lignocellulosic composites, *L. cylindrica* has been tested as a reinforcing matrix in polyester composites.²⁷ No reinforcement was observed, but the fibers act as an efficient crack deflectors because of their mat-like structure. A slight increase in the mechanical properties was observed in case of alkali treatment of luffa.²⁸

Diethylaminoethylated cellulose (DEAE-cellulose) is one of the well-known cellulose ether derivatives. It was prepared by reacting cotton with 2-chloroethyldiethylamine (CEDA) in the presence of sodium hydroxide.²⁹ DEAE-cellulose finds many applications as, for example, in chromatographic separation,^{30–32} dyes and color removal from industrial waste water,^{33,34} and ion exchangers.³⁵

So far, to the best of our knowledge, there is no published work on chemical modification of *L. cylindrica*. Also the chemical composition and structure of its main components, i.e., cellulose, hemicelluloses, and lignin, have been rarely studied in detail.^{36,37} The mat-like and highly porous structure makes this material very useful for chemical modification without the need to convert it to smaller particles or fibers, as

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in case of the other agro-based fibers. The porous structure allows removal for unreacted chemicals and byproducts easily, as well as easy purification of the product. The aim of this work is to investigate the chemical modification of *L. cylindrica* to prepare anion exchanger material through its etherification using CEDA. The chemical composition and physical properties of the different constituents of *L. cylindrica* were first investigated.

EXPERIMENTAL

Materials

L. cylindrica was soaked in hot water for 30 min and washed with running tap water before use. 2-Chloroethyl-diethylamine hydrochloride (CEDA-HCl), epichlorohydrin, NaOH, ethanol, toluene, HCl, methyl iodide, potassium sulfate, potassium nitrate, potassium hydrogen phosphate, and dioxane were reagent grade chemicals and used without any further purification.

Chemical analysis

Before chemical analysis, *L. cylindrica* was cut into small pieces, milled using 2-mm mesh screen, soaked in hot water for 45 min, extracted with 1 : 2 ethanol: toluene mixture, and finally washed with ethanol and left to air dry. The percent of extractive was determined from the weight loss due to the extraction. Klason lignin, holocellulose, pentosans, α -cellulose, and ash content were determined according to the standard method of chemical analysis of lignocellulosic materials.³⁸ For studying lignin structure in *L. cylindrica*, lignin was isolated by treatment of extractive-free luffa with a dioxane-water mixture (9 : 1) containing 0.2 mol/L HCl at 90°C for 8 h.³⁸

Characterization of *Luffa cylindrica* and diethylaminoethylated-luffa

The X-ray diffraction patterns of cellulose in *L. cylindrica* and DEAE-luffa samples were recorded using a Diano X-ray diffractometer using $K\alpha$ Co radiation at wavelength of 1.79 nm. The samples were pressed into discs of 2.5 cm diameter. A JASCO 300-E Fourier transform infrared (FTIR) spectrometer was used for obtaining the FTIR spectra using KBr disc technique. ¹H NMR spectrum of dioxane-lignin was obtained using a Jeol FTEX 270 spectrometer at 270 MHz.

Chemical modification of *L. cylindrica*

Chemical modification of *L. cylindrica* with CEDA was carried out based on the modified method of Hartmann³⁹ at different CEDA concentrations (5–25%),

NaOH concentrations (5–25%), temperatures (50–90°C), and at constant reaction time of 30 min. *L.* was first soaked in aqueous solution of CEDA for 30 min, removed from the solution and dried at 65°C for 10 min, and immersed in NaOH solution for 30 min at different temperatures. Nitrogen content of the prepared DEAE-luffa was determined according to the micro-Kjeldahl method.³⁸ Crosslinking of the DEAE-luffa with epichlorohydrin was carried out by treating the DEAE-luffa with epichlorohydrin in the presence of NaOH at 60°C for 2 h under reflux.⁴⁰ Quaternization of the crosslinked DEAE-luffa was carried out by its reflux with 10% methyl iodide in ethanol for 2 h.

Ion-exchange properties

For studying the anion-exchange properties, 0.2 g of the crosslinked and quaternized DEAE-luffa was immersed in 10 mL of the different salt solutions at different concentrations (0.01–0.1M) until equilibrium (after 24 h) at room temperature with shaking. The mixture was filtered and the concentration of phosphate, sulfate, or nitrate anions was determined in the filtrate according to the known standard methods.⁴¹ Phosphate anions were determined gravimetrically as magnesium pyrophosphate after addition of magnesium chloride and ammonia solutions. Sulfate anions were determined gravimetrically as barium sulfate after addition of barium chloride solution. Nitrate anions were determined by their reduction first to ammonia by means of zinc powder in a strong alkaline medium, followed by distilling ammonia into an excess of standard HCl solution and titrating the residual HCl using standard NaOH solution.

To study the effect of regeneration on the adsorption capacity of the crosslinked and quaternized DEAE-luffa, three portions of 20 mL of 0.01M NaOH solution was added to 0.2 g of DEAE-luffa after adsorption of the anions. The DEAE-luffa was filtered and washed with water until it was free of alkali.

RESULTS AND DISCUSSION

Chemical composition of *L. cylindrica*

Studying the chemical composition, structure, and properties of constituents of lignocellulosic materials is important, since it gives an idea about their expected reactivity toward chemical modification and possible applications of the lignocellulosic material under investigation. Luffa constituents were reported to be mainly cellulose, lignin, and hemicelluloses. It has been shown recently that hemicelluloses in luffa consist of arabinose, xylose, galactose, and glucose sugars in the molar proportions 1 : 95 : 2 : 1, and uronic acid was estimated to be about 10%.³⁷

TABLE I
Chemical Composition of *L. cylindrica* and Some Common Agro-Based and Wood Fibers⁴²

Type of fiber ^a	Holocellulose (%)	α -Cellulose (%)	Pentosans (%)	Klason lignin (%)	Ash (%)	Ethanol/benzene extractives (%)
<i>Luffa cylindrica</i>	79.5	58.3	15.0	13.6	1.8	2.2 ^b
Sisal		43–63.9	21–24	8–11	0.6–1	–
Bamboo	68.8–72	32–44	27–32	19–24	1.5–5	3.2–7.9
Flax	–	45–68	6–17	10–15	2–5	8.9
Kenaf	–	31–39	16.1	8–12.1	2–5	3.3–7.5
Jute	–	58–63	18–21	21–26	0.5–1	0.9–3.5
Bagasse	–	31.6–32.4	27.6–31.8	17.8–23	1.8–5.4	2.3–10.8
Rice straw	–	28–36.2	21–28	11.9–25.5	16.1–24.8	2.1–5.1
American beech (H)	77.0	49.0	20.0	22.0	0.4	2.0
Red maple (H)	77.0	47.0	18.0	21.0	0.4	3.0
Red alder (H)	74.0	44.0	20.0	24.0	0.3	2.0
Yellow birch (H)	73.0	47.0	23.0	21.0	0.7	2.0
White oak (H)	67.0	47.0	20.0	27.0	0.4	3.0
White fir (S)	66.0	49.0	6.0	28.0	0.4	2.0
Western larch (S)	65.0	48.0	9.0	27.0	0.4	2.0
Engleman spruce (S)	69.0	45.0	10.0	28.0	0.2	2.0

^a (H) refers to hardwood and (S) refers to soft wood.

^b Ethanol/toluene mixture was used.

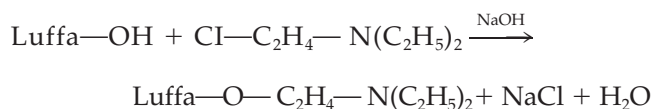
The chemical composition of the mature *L. cylindrica* used is listed in Table I. As shown in the table, *L. cylindrica* is characterized by relatively low lignin content and high α -cellulose content. The presence of lignin in the cell walls or between the fibers is known to hinder the chemical reaction of cellulose and hemicelluloses. The low lignin content of *L. cylindrica* compared with that of the other agro-based and agricultural wastes (Table I) is expected to make it easier in chemical modifications such as esterification and etherification. The α -cellulose content is remarkably high compared with that of some agro-based and wood species,⁴² as shown in Table I. The crystallinity index (CrI, calculated from the X-ray diffraction pattern of luffa) of cellulose in *L. cylindrica* was 0.67.

To study the structure of lignin in luffa, lignin was isolated from luffa using dioxane–water mixture in acidic medium. Dioxane-lignin has been widely used as one of macromolecular lignin preparations, because of the simplicity of its isolation compared to milled-wood lignin that is used for studying lignin structure. The isolated dioxane-lignin preparation affords the investigation for the delignification reaction in homogeneous systems.⁴³ Dioxane-lignin isolated from *L.*

cylindrica showed ¹H NMR spectrum (Fig. 1) indicating the presence of both syringyl and guaiacyl units, but the former type predominates. Table II shows the assignment of the ¹H NMR signals of the dioxane-lignin. The estimation of the various types of protons per C₉ structural unit of lignin has been conducted according to the previous studies on the different types of lignin.^{44,45}

Chemical modification of *L. cylindrica* with CEDA

L. cylindrica was soaked in CEDA and then immersed in NaOH solution. The reaction takes place between CEDA and luffa constituents that bear hydroxyl groups, i.e., cellulose, hemicelluloses, and lignin, according to the following equation:



In literature, there are different reaction conditions reported for the use of CEDA for modification of

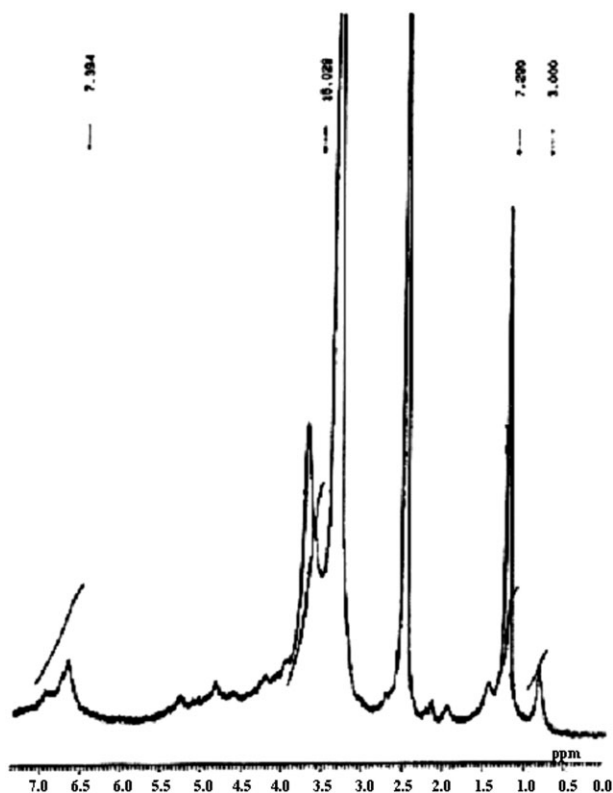


Figure 1 ^1H NMR spectrum of dioxane-lignin isolated from *L. cylindrica*.

cotton to prepare the well-known DEAE-cellulose derivative. So, the effects of the different reaction parameters on the extent of the modification of luffa were studied to optimize the reaction to obtain the highest possible reaction yield. The FTIR spectra of different DEAE-luffa samples are shown in Figure 2. As shown in the figure, only a slight change in the FTIR spectra was observed because of the introduction of the DEAE group into the luffa constituents. This is expected, since the only difference between the unreacted and reacted luffa is the presence of the C—N and CH_3 groups in the latter. Unfortunately, the C—N absorp-

TABLE II
 ^1H NMR Chemical Shift Assignment of the Dioxane-Lignin Isolated from *L. cylindrica*

Chemical shift of the maximum (ppm)	Main assignment
2.5	DMSO
3.5	Residual water
6.7	Aromatic H in syringyl unit
7	Aromatic H in guaiacyl unit
5.3	H of xylane residue
4.8	H_α and H_β of β -O-4 structure
3.75	H of methoxy group
1.3	Hydrocarbon proton
0.8	Highly shielded aliphatic H

tion band could not be clearly detected, since it is usually in the region from 1050 to 1200 cm^{-1} , which is the same region of the C—O—C bending vibrations of cellulosic materials. There is a noticeable increase in intensity of the methylene group absorption band at about 2900 cm^{-1} due to the methylene groups of DEAE moieties. Also, a small shoulder at about 1370 cm^{-1} was observed in the FTIR spectra of DEAE-luffa. This may be corresponding to the bending vibration of the introduced methyl groups in the DEAE moieties. The O—H adsorption band at 3400 cm^{-1} showed insignificant change in intensity. This means that a considerable number of hydroxyl groups were still free and unreacted.

The previous studies^{33,46–48} on preparation of DEAE-cellulose from cotton showed relatively low nitrogen content values similar to those found in this study on luffa. The nitrogen content values of the prepared DEAE-cellulose were about 0.4–1.2%. These values correspond to a low degree of substitution (DS ~ 0.2 for 1.2% nitrogen), which can be attributed to the bulkiness of the DEAE group. On comparing the extent of the reaction on luffa to that published on cellulose modification with DEAE, it is obvious that comparable extent of reaction could be obtained without removal of lignin and hemicelluloses from luffa. The highest nitrogen content value (0.87%) obtained for the DEAE-luffa was at 70°C using CEDA concentra-

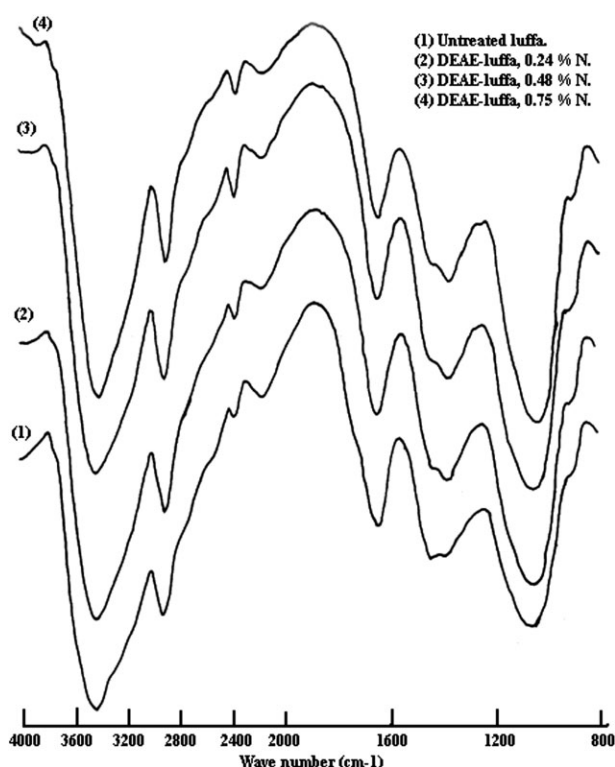


Figure 2 FTIR spectra of DEAE-luffa samples having different nitrogen content. (1) Untreated luffa; (2) DEAE-luffa, 0.24% N; (3) DEAE-luffa, 0.48% N; (4) DEAE-luffa, 0.75% N.

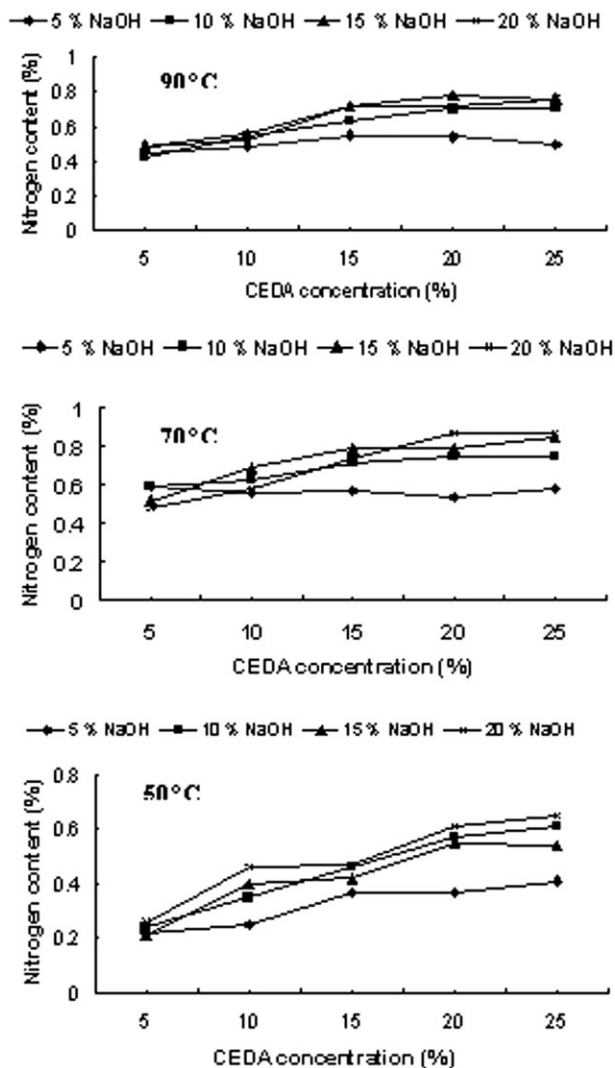


Figure 3 Effect of CEDA concentration on nitrogen content of *L. cylindrica* at different NaOH concentrations and reaction temperatures.

tion of 15–25% and NaOH concentration of 20%. Figures 3–5 show the effects of the different reaction conditions used on the nitrogen content of the produced DEAE-luffa, i.e., on the extent of reaction.

Effect of CEDA concentration

Figure 3 shows the effect of CEDA concentration on the nitrogen content of the DEAE-luffa at different NaOH concentrations and reaction temperatures; the reaction time was kept constant at 30 min. As seen in the figure, the effects of the reaction parameters are not simple and depend on each other. At low reaction temperature (50°C), increasing CEDA concentration generally resulted in increasing the nitrogen content at the different NaOH concentrations. Also, at this reaction temperature, the nitrogen content of all the produced DEAE-luffas were relatively low. At higher

reaction temperatures (70 and 90°C), there is no significant increase in nitrogen content on increasing CEDA over 15–20%. Increasing CEDA concentration should be accompanied with increasing NaOH concentration to increase the extent of the reaction.

Effect of NaOH concentration

Sodium hydroxide added during the reaction has two roles: (1) it causes swelling of the fibers, especially cellulose, and thus facilitates the penetration of CEDA into the fibers and the crystalline cellulose regions; (2) upon the reaction of luffa constituents with CEDA, NaOH reacts with the liberated HCl and consequently drives the reaction to the forward direction. In addition, part of NaOH is consumed in neutralizing the CEDA-HCl. The alkali added is expected to cause also dissolution of fractions of the different luffa constitu-

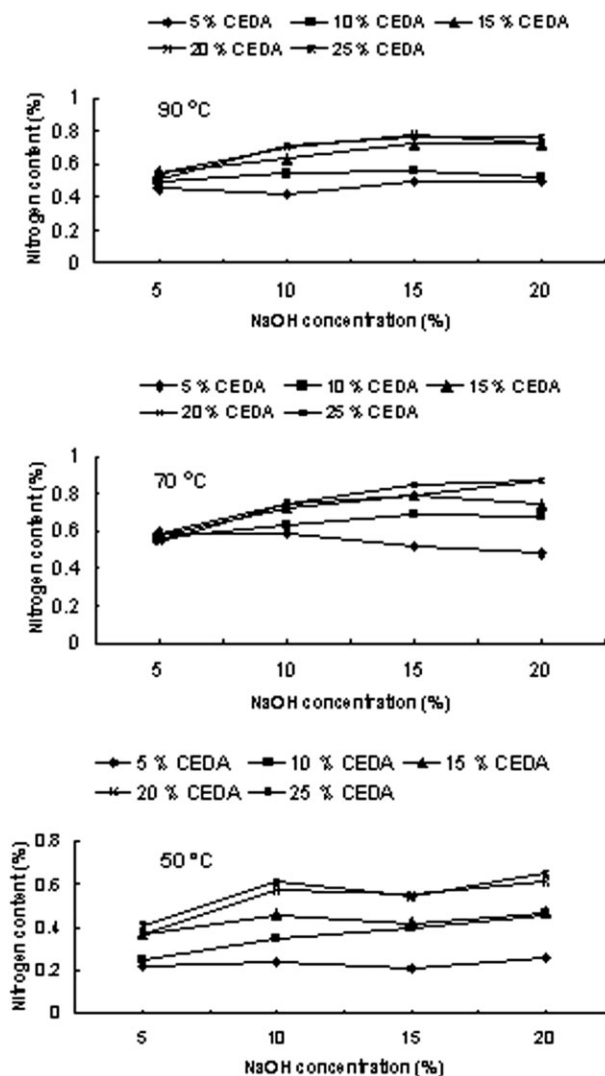


Figure 4 Effect of NaOH concentration on nitrogen content of *L. cylindrica* at different CEDA concentrations and reaction temperatures.

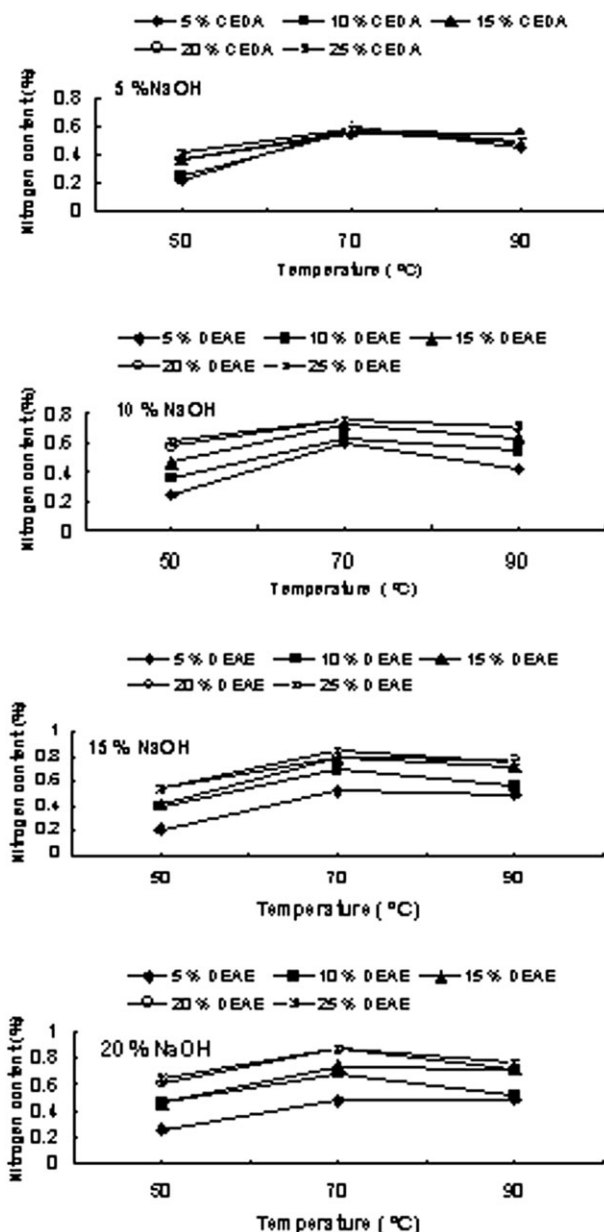


Figure 5 Effect of reaction temperature on nitrogen content of *L. cylindrica* at different NaOH and CEDA concentrations.

ents. Figure 4 shows the effect of NaOH concentration on the nitrogen content of the prepared DEAE-luffa. At low temperature (50°C), there was insignificant increase in nitrogen content on increasing NaOH concentration above 10%. At 70°C, increasing NaOH concentration resulted generally in an increase in the nitrogen content of the DEAE-luffa in the case of using high concentrations of CEDA (20–25%). At 90°C, no increase or a slight decrease in nitrogen content was observed on using NaOH concentration higher than 15% at the different CEDA concentrations. The slight decrease in nitrogen content may be due to dissolution of the DEAE-luffa constituents, especially DEAE-cellulose and DEAE-hemicelluloses.

Crosslinking of luffa constituents before etherification using epichlorohydrin may be useful in decreasing their dissolution by the action of alkali and temperature. But this will be on the expense of number of available hydroxyl groups for etherification. In this work, due to the relative bulkiness of the DEAE group and to achieve high extent of etherification, crosslinking was carried out after etherification. NaOH is used for regeneration of DEAE-luffa after its use for anion removal, and protecting of DEAE-luffa constituents from the possible dissolution by alkali is essential.

Effect of reaction temperature

Figure 5 shows the effect of reaction temperature on the nitrogen content of the prepared DEAE-luffa at different NaOH and CEDA concentrations after 30 min of reaction. From the figure, it could be concluded that the optimum reaction temperature was 70°C. Increasing the reaction temperature above 70°C had no significant effect, or caused a slight decrease in the nitrogen content of the prepared DEAE-luffa because of possible dissolution of the DEAE-luffa constituents as mentioned earlier.

Effect of modification on the supramolecular structure of cellulose in *L. cylindrica*

The effect of the modification of luffa on the crystallinity of cellulose was studied using X-ray diffraction technique. Figure 6 shows X-ray diffraction patterns of selected DEAE-luffa samples prepared at 70°C. The CrI was calculated according to Clark and Terford,⁴⁹ and the results are listed in Table III. Cellulose in untreated luffa shows typical cellulose I diffraction pattern with reflections at $2\theta = 25.5$ and $2\theta = 17.3$ and CrI of 0.67. The reflection peak at $2\theta = 25.5$, which was derived from the 002 plane of the cellulose I lattice, has been broadened on increasing the concentration of the NaOH used and on increasing the extent of the reaction. At 20% NaOH concentration, the reflection peak at $2\theta = 25.5$ split into two peaks at $2\theta = 25$ and $2\theta = 23.5$, indicating the gradual transformation to cellulose II structure. At the same time, the intensity of the peak around $2\theta = 17.3$, which is assigned to the reflection of the 101 and $10\bar{1}$ lattice planes of cellulose I, gradually decreased and broadened and became very broad and weak at high NaOH concentration. As shown in Table III, a slight increase in the CrI was found on using lower concentrations (5 and 10%) of NaOH. It is known that NaOH solution of low concentration (~8%) is more suitable for dissolution of the amorphous hemicelluloses. At higher NaOH concentration (15%) and higher nitrogen content of the prepared DEAE-luffa, the crystallinity decreased because of the alteration in the structure of cellulose in luffa. At the highest NaOH concentration used (20%),

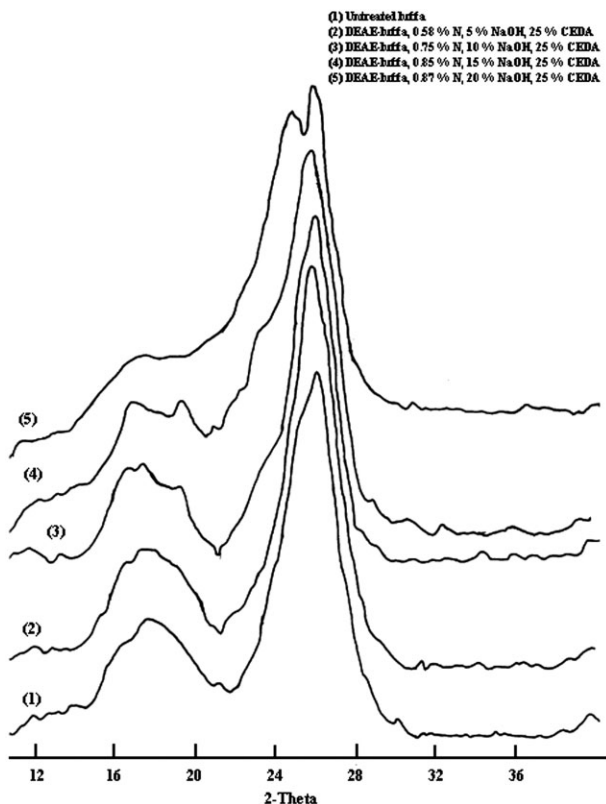


Figure 6 X-ray diffraction patterns of different DEAE-luffa samples prepared at 70°C. (1) Untreated luffa; (2) DEAE-luffa, 0.58% N, 5% NaOH, 25% CEDA; (3) DEAE-luffa, 0.75% N, 10% NaOH, 25% CEDA; (4) DEAE-luffa, 0.86% N, 15% NaOH, 25% CEDA; (5) DEAE-luffa, 0.87% N, 20% NaOH, 25% CEDA.

an increase in CrI is noticed in spite of the nitrogen content obtained nearly similar to that of the sample prepared using 15% NaOH. This is probably due to the increasing dissolution of the amorphous constituents (cellulose short chains and hemicelluloses) on using 20% NaOH solution.

Ion exchange capacity of DEAE-luffa

To test the ion-exchange capacity of the prepared DEAE-luffa, a sample which exhibited high nitrogen content was chosen (0.85% nitrogen and prepared us-

TABLE III
Crystallinity Index (CrI) of DEAE-luffa Calculated from the X-ray Diffraction Patterns

Reaction conditions	Nitrogen content (%)	CrI
None	–	0.67
5% NaOH, 25% DEAE, 70°C	0.58	0.70
10% NaOH, 25% DEAE, 70°C	0.75	0.70
15% NaOH, 25% DEAE, 70°C	0.85	0.62
20% NaOH, 25% DEAE, 70°C	0.87	0.76

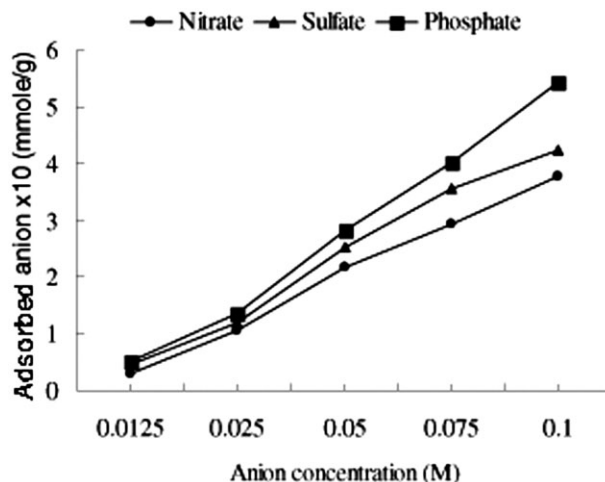


Figure 7 Adsorption of the different anions by DEAE-luffa (nitrogen content 0.87%) at room temperature after 24 h.

ing 15% NaOH, 20% CEDA, and at 70°C). The DEAE-luffa sample was first crosslinked with epichlorohydrin since anion exchangers are usually regenerated with NaOH solutions, which may cause leaching of DEAE-luffa constituents. After crosslinking, the sample was reacted with methyl iodide to prepare the quaternary ammonium salt, which is known as a strong anion exchanger. Crosslinked and quaternized DEAE-luffa was regenerated with 0.01N NaOH, and the anion-exchange capacity toward removal of nitrate, phosphate, and sulfate anions was tested at room temperature after shaking for 24 h. Figure 7 shows the adsorption of the different anions by the DEAE-luffa at different concentrations of the anions. As shown, the maximum adsorption (mmole/g) of nitrate and sulfate anions was lower than the amount of the introduced DEAE groups (DEAE-luffa nitrogen content 0.85% is equivalent to ~0.62 mmole of DEAE per gram of luffa), while the maximum adsorption of

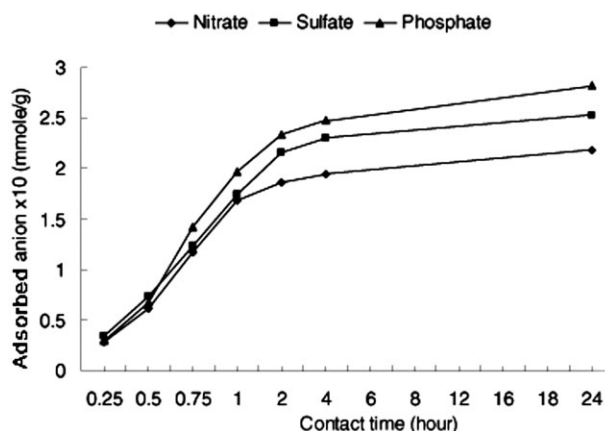


Figure 8 Effect of contact time on the quantity of adsorbed anions using 0.05M solutions.

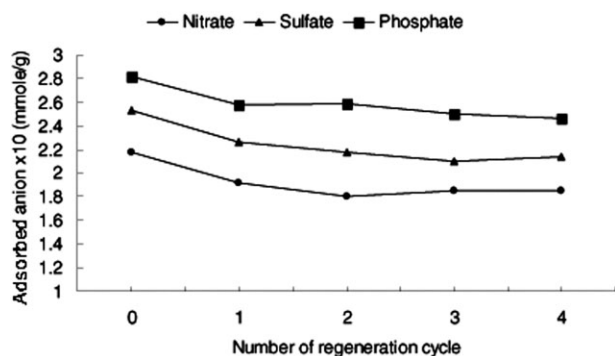


Figure 9 Effect of regeneration of DEAE-luffa (nitrogen content 0.87%) on its adsorption capacity after 24 h using 0.05M solutions.

phosphate anions was close to the amount of the introduced DEAE groups. This means that not all the quaternized functional groups could be exchanged with the sulfate and nitrate anions. At maximum adsorption, DEAE-luffa showed the following order in affinity toward the anions: phosphate > sulfate > nitrate. The lowest affinity toward the nitrate anions is probably due to the one negative charge that they carry while both sulfate and hydrogen phosphate anions has two negative charges. The negative charges on HPO_4^{2-} anions are stronger than those on SO_4^{2-} anions because of the presence of two double bonds in the structure of the sulfate anions, while there is one double bond in the structure of hydrogen phosphate anions.

Rapid adsorption of pollutants onto the ion-exchange material and attaining fast equilibrium are desired properties in addition to its high adsorption capacity. The effect of contact time on adsorption capacity of the DEAE-luffa was studied using 0.05M anion concentration, and the results are shown in Figure 8. As shown, the majority of adsorption took place during the first 2 h and relatively slight increase in adsorption occurred at longer soaking time.

Regeneration of DEAE-luffa

Recovery of the adsorbed anions and repeated usability of the exchangers is important in reference to the practical applications of treatment of industrial effluents. To demonstrate the reusability of the DEAE-luffa, the adsorption-desorption cycle was repeated five times, and the effect of regeneration is shown in Figure 9. The adsorption capacities did not change noticeably. The slight decrease in the adsorption capacity in the first two cycles may be due to the dissolution of DEAE-hemicelluloses and short chains, in spite of the crosslinking made using epichlorohydrin.

CONCLUSIONS

L. cylindrica is characterized by high α -cellulose content and relatively low lignin content. The lignin in *L.*

cylindrica contains both syringyl and guaiacyl units, but the former type predominates. Strong anion exchanger could be prepared using *L. cylindrica* through etherification, crosslinking, and quaternization. The etherification affected the supramolecular structure of luffa as seen from the X-ray diffraction and was not confined to surface modification. Quaternized DEAE-luffa showed capability of adsorption of nitrate, sulfate, and phosphate anions and could be repeatedly used without significant effect on its adsorption capacity.

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