Desalination and Water Treatment
www.deswater.com

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doi: 10.1080/19443994.2012.734685

51 (2013) 2153–2161
February

Taylor & Francis
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Multicomponents adsorption of modified cellulose microfibrils

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Received 13 October 2011; Accepted 3 September 2012

ABSTRACT

Jute has been used as a raw material to chemically modified cellulose microfibres. For this purpose three chemical treatments were used: mercerization with NaOH, acetylating with nitric acid and acetic acid and finally hydrolysis with sulphuric acid. The isolated microfibrils were characterized by Fourier transform infrared spectroscopy (FTIR) and Technical Association of the Pulp and Paper Industry standards have been applied before and after chemical treatment to determine the composition of the cellulosic materials which was decreased considerably the lignin content from 17 to 1.7%. The microfibrils were treated with palmitic acid to graft a long hydrocarbon chain and able to retain organic molecules such as toluene or benzene in water. In this way, after elimination of water from the cellulose microfibrils by azeotropic distillation; palmitic acid, *N*-*N*′-Dicyclohexylcarbodiimide and 4-(Dimethylamino) pyridine catalyst were added to esterify cellulose microfibrils. Treated fibres were characterized by FTIR to follow the ester carbonyl formation peak and contact angle measurements to determine the decrease in the hydrophilic character of the initial untreated fibres. The adsorption capacity of these microfibrils has been studied using various solutions of different organic components, benzene or toluene, and then, we have studied the retention capacity in a multicomponent solution, i.e. with two organic components in the same solution.

Keywords: Adsorption; Modified cellulose; Microfibrils; Multicomponents

1. Introduction

Despite considerable advances in the water treatment area, removal of certain kinds of products to meet the current rules still raises some issues and remains a concern. This is the case of organic compounds, such polyphenols, aromatic compounds and metal ions, which are considered the most toxic to living species. The chemical industry, household waste and agriculture are probably the main sources of this pollution. In the absence of any treatment, the organic compounds and persistent organic pollutants, such certain pesticides, accumulate in the water and promote the risk of irreversible pollution.

In the last few years, numerous studies have been performed to develop a cheaper and biodegradable adsorbent process containing natural polymers for the water decontamination [1–4]. The use of cellulose as a substrate of adsorption is not recent. Cellulose is a wide-spread natural element, since it is the most abundant renewable organic biomolecule, as it forms the bulk of terrestrial biomass and can be easily degraded biologically. Previous studies highlighted the ability of this natural material to fix a number of organic compounds by adsorption [5]. It has also

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demonstrated the ability of cellulose to fix metal ions by adsorption [6–8]. However, the adsorption characteristics of native cellulose are not constant. It varies according to the origin of the cellulose and the preliminary treatments. Similarly, the adsorption capacity (for organic compounds as well as metal ions) remains very low compared to the activated carbon or zeolite. This effect is due to the low affinity to establish specific interactions with contaminants. The increase of the hydrophobicity of the adsorbent is a significant aspect, greater hydrophobicity generate a greater affinity with contaminants.

Adsorption characteristics of cellulose can be extended significantly by chemical modification of fibre surface. This can be achieved by introducing chemical groups that exhibit a high affinity for chemical species in aqueous solution such as acrylamide and acrylic acid to adsorb water, chitin to adsorb heavy metals, or sorption of Cu^{2+} ions by cellulose graft copolymers [9–11]. These modifications are made possible by special structure of cellulose.

Based on this principle, cellulose microfibrils have been used in this work aiming to obtain a low-cost, renewable and biodegradable microfibril material having large surface area for solute adsorption. Jute fibres have been used as raw materials for cellulose microfibrils isolation. Jute is a long, soft, shiny vegetable fibre. It is produced from plants of the genus *Corchorus*, which has been classified in the family *Tiliaceae*. For the elaboration of microfibrils three chemical treatments were used. The first treatment was a mercerization with NaOH, the second treatment was acetylating process and the final process was hydrolysis with sulphuric acid. The obtained jute microfibrils were treated with palmitic acid in order to obtain an ester with a long hydrocarbon chain able to retain organic molecules in water [12]. Jute microfibrils and jute-modified microfibrils were characterized by using an Fourier transform infrared spectroscopy (FTIR), thermogravimetrical analysis (TGA) and contact angle measurements.

2. Experimental section

2.1. Materials

Natural jute fibres supplied by Celesa have been used and microcrystalline cellulose powder (Avicel) supplied by Sigma-Aldrich has been applied as reference for comparative study. The composition of jute fibres which was determined according to Technical Association of the Pulp and Paper Industry (TAPPI) standards is shown in Table 1.

2.2. Extraction of microfibrils

The extraction of microfibrils of jute was a three-step process consisting of a mercerization, acetylating and hydrolysis. Similar methods have been used in previous works for the extraction of cellulose microfibrils [13,14].

Jute fibres were ground in a hammer mill and sieved to obtain the 4 mm size fraction, free of impurities such as stones, sand and dust.

After the pre-treatment, the first step of microfibril isolation was a mercerization process in which 5 g of jute fibres were added to a solution containing 100 ml of NaOH (7.5%) and these fibres were heated to boiling point and treated for 90 min with agitation. At the end of this treatment the fibres were washed and dried. This process eliminates the non-cellulosic materials such as lignin. In the second step, acetylating was carried out destroying microstructure, for this, 0.6 g of mercerized fibres was added to a solution containing 2 ml of nitric acid and 12 ml of acetic acid and this solution was heated to boiling point and treated for 30 min with agitation. Next, the fibres were washed and dried. The final step consist of a hydrolysis process, in which 1 g of treated fibres was added to a solution containing 8.75 ml of H_2SO_4 and then heated to 45°C for 1 h. Finally, the fibres were washed, dried and kept in a plastic bag to protect from moisture.

The composition of jute microfibrils, after the three treatments, was determined according to TAPPI standards, the data are shown in Table 2. In this, it was observed that content of lignin was reduced considerably.

2.3. Functionalization of Avicel and jute microfibrils

The functionalization of the cellulose (Avicel) and jute microfibrils was carried out by esterification of the fibres through an elimination of water by azeotropic distillation, followed immediately by addition of palmitic acid, a dehydration agent *N-N′* dicyclohexyl-

Table 1
Composition of the jute fibre

Composition (%)	Fat and wax	Pectin	Lignin	Hemicelluloses	α-Cellulose
Jute fibre	8.3 ± 0.12	5.4 ± 0.77	17.2 ± 0.98	33.5 ± 0.55	46.2 ± 0.73

Table 2
Composition of the jute microfibrils

Composition (%)	Fat and wax	Pectin	Lignin	Hemicelluloses	α-Cellulose
Jute microfibrils	2.9 ± 0.11	3.4 ± 0.81	1.7 ± 0.23	33.1 ± 0.02	61.7 ± 0.14

carbodiimide (DCC) and the catalyst 4-(dimethylamino)pyridine (DMAP) [15–18], and putting all together in a toluene/DMF (60/40) mixing to 80°C for 3 h with reflux.

Cellulose fibres (3 g) were swelling in hot water, filtered and then introduced in the flask containing 100 ml of a mixture of toluene/DMF (60/40 v/v). The solution was heated under reflux for the elimination of water remained on the fibres, then it was evacuated by azeotropic distillation in 3 h. Immediately 5 g of a dehydration agent DCC, 6 g of palmitic acid and 0.5 g of catalyst DMAP were added and the reaction was carried out for 3 h and at 80°C. Finally, the obtained product was cooled and then purified by Soxhlet extraction with THF/Ethanol (50/50 v/v) for 24 h. The obtained modified microfibrils were dried and kept in plastic bags.

2.4. Instrumental analysis

FTIR has been used to observe the reduction of lignin in jute fibres, and to check the modification of Avicel and jute microfibrils, analysing the characteristics bands of lignin and the esters. The FTIR spectra were obtained from KBr pellets with a Nicolet Nexus FTIR spectrophotometer used in a transmission mode with a resolution of $8\,\mathrm{cm}^{-1}$ with 20 scans for each specimen.

TGA was used to observe the reduction of hydroxyl groups after modification, verifying the good esterification of Avicel and microfibrils. TGA was performed using a Mettler-Toledo thermal analyzer heating from 25 to 800°C at heating rate around 1°C/min. The 10 mg of each dried simple were weighed for the experiment.

Contact angle measurements were also carried to determine the hydrophilic character of each sample, after and before the esterification treatment. These measurements were also carried out with water and with each of fibre uniform pellets. Contact angle measurements were performed using a Dataphysics Contact angle system OCA 20.

2.5. Batch adsorption studies

Solute adsorption experiments under batch condition were performed at room temperature, adding organic solute—toluene 1 mmol/L—in a water solution containing 1 wt% of fibres. The sample concentrations were measured every 30 min during 500 min to the equilibrium time using Jasco V-630 spectrophotometer.

2.6. Batch adsorption studies in a multicomponent solution

The study of the adsorption capacities of the modified microfibrils in a solution of two organic compounds is based on law of Beer–Lambert [19], which defines that the amount of light adsorbed in a determined frequency by the compound is directly proportional to the concentration of same compound in solution. The adsorption experiments were carried out using the same methodology and conditions used for a single component.

$$A = \varepsilon\, I\, C$$

A = Adsorbance
ε = molar absorption constant
l = optical path length
C = concentration of the absorbing substance

This law is used to obtain a mathematical relationship between the adsorption and concentration.

Each of the components present in the solution has a characteristic wavelength, given its particular structure. The absorbance is an additive property, i.e. in solutions containing more than one species; the total adsorbance is the sum of the individual adsorbance's of each species.

$$A_{\mathrm{tot}} = A_{\mathrm{benzene}} + A_{\mathrm{toluene}} = \varepsilon_{\mathrm{ben}}\, IC_{\mathrm{ben}} + \varepsilon_{\mathrm{tol}}\, IC_{\mathrm{tol}}$$

In order to define the concentrations of each pollutant, the adsorptive molar of each compound in both wavelengths must be defined before, thus establishing the amount of light absorbed by each compound in each of the characteristic wavelengths.

This will require preparing a solution for each component and passing the samples of each solution, for the corresponding wavelengths. So, we get two values of molar absorptive compound, which make reference to the mentioned wavelengths.

For this reason, different solutions with a given concentration for each pollutant have been prepared. These dissolutions have been measured at two wavelengths to obtain two molar absorptivities for each pollutant.

After obtaining the molar absorptivities, the concentrations of an unknown solution may be determined. The sample will be passed by two characteristic wavelengths to obtain two values of absorbance. The adsorptive molars have already been obtained previously and the only unknowns in the equation are the concentrations of toluene and benzene.

$$A_{tot(254)} = \varepsilon_{ben(254)}\, IC_{ben} + \varepsilon_{tol(254)}\, IC_{tol}$$

$$A_{tot(261)} = \varepsilon_{ben(261)}\, IC_{ben} + \varepsilon_{tol(261)}\, IC_{tol}$$

$A_{tot(254)}$ = Adsorbance at 254 nm
$\varepsilon_{ben(254)}$ = molar absorption constant at 254 nm
$\varepsilon_{tol(254)}$ = molar absorption constant at 254 nm
$A_{tot(261)}$ = Adsorbance at 261 nm
$\varepsilon_{ben(261)}$ = molar absorption constant at 261 nm
$\varepsilon_{tol(261)}$ = molar absorption constant at 261 nm
I = optical path length
C_{ben} = Benzene concentration
C_{tol} = Toluene concentration

3. Results and discussion

3.1. FTIR spectra

The treatment for microfibrils extraction has removed the characteristic lignin-associated band at 1,735 cm^{-1} obtaining microfibrils rich in cellulose as it can be observed in Fig. 1.

In the jute plant spectra, the signals at 3,350, 2,936 and 2,890 cm^{-1} are characteristic of stretching vibrations of OH and CH groups, respectively, when the signal of 2,936 cm^{-1} corresponds to a CH_3 group and the signal of 2,890 cm^{-1} corresponds to a CH_2 group. The vibration signal of 1,735 cm^{-1} is due to vibrations of C=O characteristic of lignin. The peak at 1,645 cm^{-1} is attributed to the bending mode of the absorbed water. The band at 1,424 cm^{-1} corresponds to a CH_2 bending and the one at 1,230 cm^{-1} is originated from the OH in plane-bending cellulose [20,21]. The adsorption band at 1,160 cm^{-1} is attributed to C–O antisymmetric bridge stretching. Finally, the peak at 890 cm^{-1} is characteristic of β-glycosidic linkages between the glucose units [22].

Comparing commercial microcrystalline cellulose (Avicel), before and after treating with palmitic acid (Fig. 2), observed that an esterification reaction is complete and a new peak can be found at 1,745 cm^{-1}, corresponding to a carbonyl vibration of the ester group formed in the reaction.

In the case of the M_f spectra comparing with modified microfibrils spectra, were observed that an esterification reaction was complete too, but in this case, a new peak can be found at 1,745 cm^{-1}, which is less intense comparing with a modified Avicel spectra.

3.2. Thermogravimetric analysis (TGA)

Thermograms of commercial microcrystalline cellulose (Avicel) and jute microfibrils (Fig. 3) show a similar degradation temperatures but the Avicel has a lower residual weight.

Comparing thermograms when these fibres are treated with palmitic acid, we observed that the modified fibres have a higher degradation temperatures and the residual mass after heating samples up to

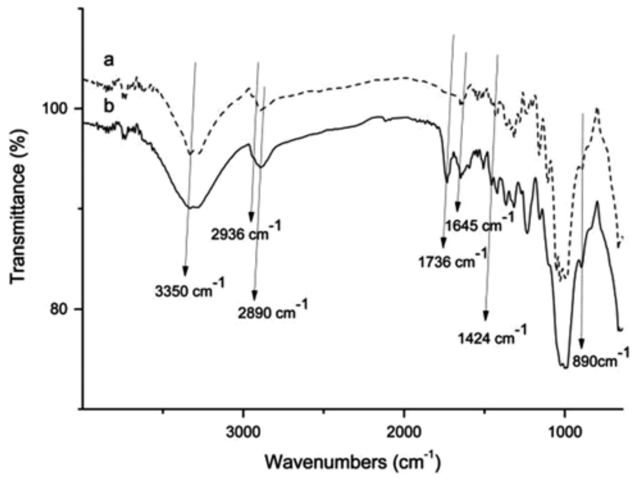

Fig. 1. FTIR spectra of (a) microfibrils (M_f) and (b) jute plant.

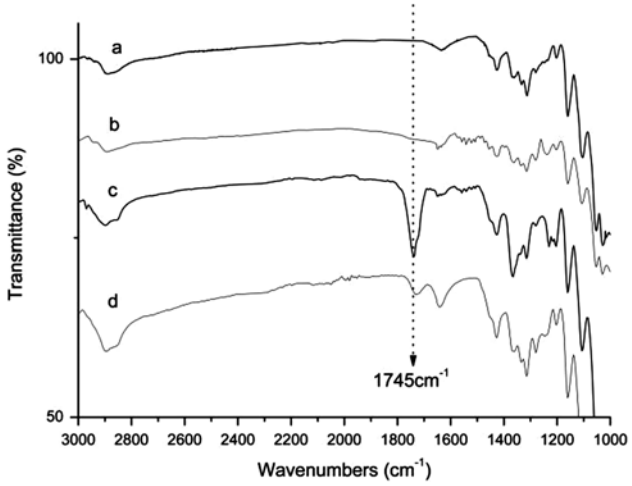

Fig. 2. FTIR spectra of (a) Avicel, (b) M_f, (c) modified Avicel and (d) modified M_f.

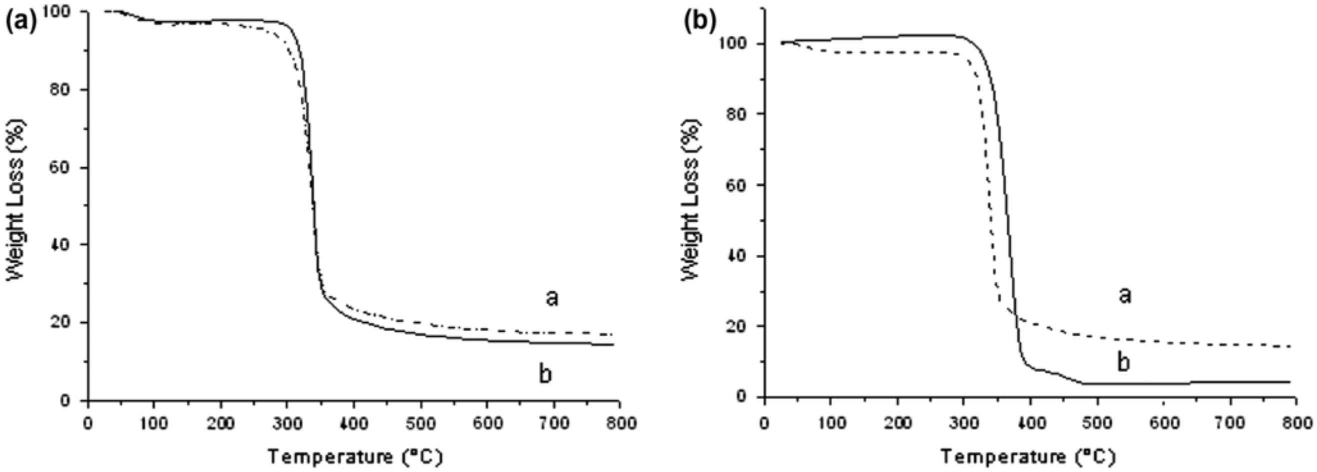

Fig. 3. Thermograms comparing different fibres before and after treatment. (a) a—Avicel and b—*M*$_f$; (b) (a) Avicel and (b) Modified Avicel.

700℃ are lower. This behaviour reveals that some hydroxyl groups in the cellulosic chains have reacted with the palmitic acid to form the corresponding ester.

3.3. Contact angle measurements

In Table 3, it can be observed that before treatment commercial microcrystalline cellulose (Avicel) has a lower contact angle value because of the fact that is a pure cellulose sample, while jute M_f containing residual non-cellulosic substances has a higher contact angle value [23,24].

The hydrophobic character of the fibres is a parameter that influences the adsorption capacity. The adsorbent hydrophobicity increase is a significant parameter to measure the pollutant affinity. After the treatment, the hydrophobic character of the fibres is higher because of the esterification process (Fig. 4). The most hydrophobic samples are those which have a higher cellulosic content, since pure cellulose shows a higher number of free hydroxyl groups on its structure that can react with palmitic acid.

3.4. Batch adsorption studies

The capacity of adsorption of fibres after the esterification process is higher comparing to fibres before modification. Pure cellulose sample retention capacity is lower than the jute microfibrils as expected taking into account the results obtained for contact angle measurements. In the case of Avicel and microfibrils before modification, the capacity of retention is less than 100 μmol of toluene per g of fibre. Jute microfibrils have non-cellulosic materials and the retention capacity of these fibres is higher than Avicel because these non-cellulosic materials improve the hydrophobic character of the microfibrils, increasing their adsorption capacity [25–28]. Microfibrils adsorbed 69 μmol/g and Avicel 61 μmol/g when the equilibrium is reached.

Table 3
Contact angle values for the different fibres

	Avicel	Modified Avicel	Microfibrils	Modified microfibrils
θ	34.17 ± 2.74	82.06 ± 2.79	57.44 ± 1.15	76.31 ± 1.33

When the fibres are modified the retention capacity increased considerably, and the velocity of retention is considerably higher too. The jute microfibrils after modification adsorbed around 485 μmol of toluene and modified Avicel around 580 μmol of toluene per g of fibre. The difference of the two fibres is due to the presence of the non-cellulosic material, since they hinder the reaction, the cellulose pure sample's, by having more links OH, react better with palmitic acid and gives a better esterification.

In order to determine the capacity of the modified fibres to trap organic compounds from aqueous solutions, Langmuir adsorption isotherms were established (Fig. 5).

The experiments were carried out with a contact time of 24 h.

It can be observed that the adsorption capacity increases until reaching the concentration of 1 mmol/L, then the increase is less appreciable until reaching the equilibrium concentration.

The initial slope of the adsorption isotherms varies significantly with the fibres; this behaviour can mean a different affinity between solute and modified fibres,

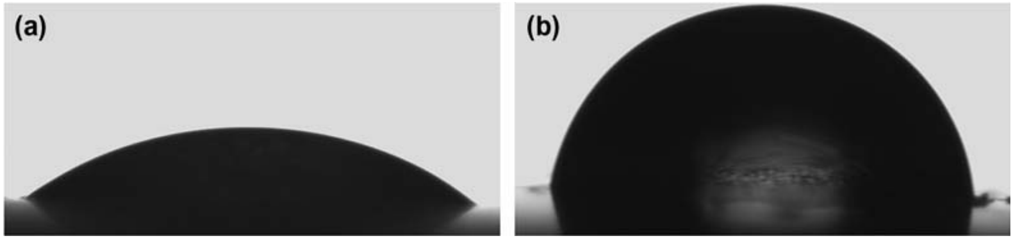

Fig. 4. Contact angle pictures (a) microfibrils and (b) modified microfibrils.

because this affinity depends on the chemical structure.

The experimental results are confirmed by the linear curve of C_{sol}/Q_{ads} ratio as a function of C_{sol}, where Q_{ads}, Q_{ads}^{max} and C_{sol} are, respectively, the adsorbed amount, the equilibrium solute concentration and the maximum adsorbed amount per unit mass of the substrate. K is the Langmuir equilibrium constant related to the energy of adsorption. The experimental values of the Langmuir constants were determined using the linear form of the equation:

$$\frac{C_{sol}}{Q_{adsol}} = \frac{1}{KQ_{ads}^{max}} + \frac{C_{sol}}{Q_{ads}^{max}}$$

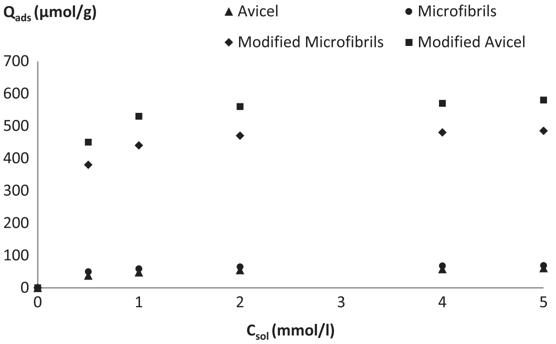

Fig. 5. Langmuir isotherms of toluene onto different fibres.

Table 4
Langmuir constants of toluene adsorption onto different fibres

	Q_e (exp) (μmol/g)	Q_e (calculated) (μmol/g)	K_2 (L mol^{-1})	R^2
Avicel	61	64	2,889	0.99
Microfibrils	69	71	4,633	0.99
Modified Avicel	580	588	18,889	0.99
Modified microfibrils	485	500	6,667	0.99

The adsorption equilibrium constant K, as well as the maximum concentration of the solute uptake, is summarized in Table 4.

The steep rise of the adsorption isotherm and the increment of values of Langmuir constant denote the high affinity of the substrate toward the efficient trapping of the dissolved organic compound in aqueous solutions when the fibres are modified.

The adsorption kinetic of toluene in different fibres before and after modification is represented in Fig. 6.

The relatively long adsorption time denotes the slow diffusion mechanism of the organic solute molecule inside the microporous structure of the fibres. Nevertheless, the sorption process seems to be rapid during the first phase although retention rate decreases significantly in the second part to achieve the adsorption equilibrium at about 500 min. The fast phase sorption is probably related to the adsorption by the external area or the fibres pore, whereas the second phase is associated with the diffusion of the solute in the inner part of the fibres micropore.

In order to study the specific rate constant of solute adsorption on fibres, the pseudo-first- and second-order equations were used. The first-order rate expression of Lagergren [29] is given as:

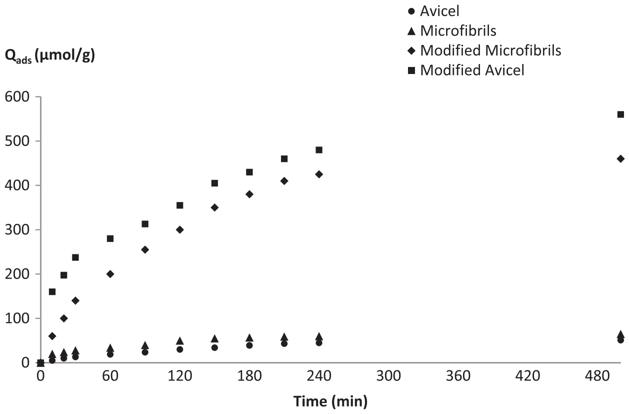

Fig. 6. Kinetic data of toluene adsorption onto different fibres.

$$\mathrm{Log}(Q_e - Q_t) = \mathrm{Log}Q_e - \frac{K_1}{2.303}t$$

Q_e = amount adsorbed at equilibrium
Q_t = amount adsorbed at any time
K_1 = the rate constant of first-order adsorption
t = time

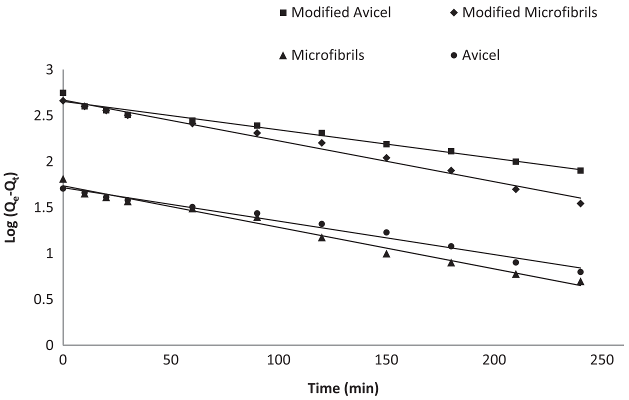

Fig. 7. Plot of pseudo-first-order model to adsorption of toluene onto different fibres.

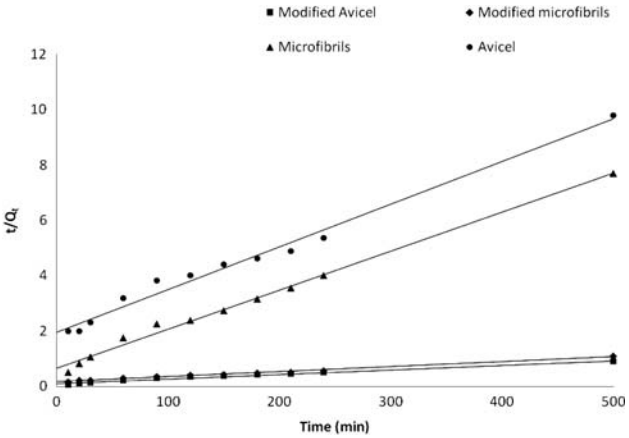

Fig. 8. Plot of pseudo-second-order model to adsorption of toluene onto different fibres.

The second-order kinetic model [30] is expressed as:

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e}$$

Q_e = amount adsorbed at equilibrium
Q_t = amount adsorbed at any time
K_2 = the rate constant of second-order adsorption
t = time

The plot of $\log(Q_e - Q_t)$ vs. t do not display a linear behaviour over the whole range of contact time indicating that the first-order model is only suitable for the initial stage of the adsorption process (Fig. 7). The straight lines in plot of t/Q_t vs. t (Fig. 8) show a good agreement of experimental data with second-order kinetic model for the different solutes. The obtained results are shown in Table 5.

3.5. Multicomponent batch adsorption studies

Two organic compounds (toluene and benzene) have been used in multicomponent batch adsorption studies. The adsorption capacity of toluene with different fibres was studied in this work, and before studying the adsorption capacity with two components, briefly the retention capacity of modified fibres with benzene has been investigated.

The driving force for the adsorption process is expected to be largely governed by van der Waals interactions between the grafted chains and the organic solute. Therefore, any factor increasing these interactions will contribute to an enhancement of the adsorption capacity [31].

Both compounds have a similar polarity in the multicomponent solution. On the other hand, the two compounds have small molar volumes and therefore does not adversely affect to the adsorption. The lower water solubility of toluene can be the factor that most

Table 5
Kinetic parameters of toluene adsorption onto different fibres using pseudo-first-order and second-order models

	Pseudo-first-order model		Pseudo-second-order model			
	K_1 (min^{-1})	R^2	Q_e (exp) (μmol/g)	Q_e (calculated) (μmol/g)	K_2 (g $\mu\mathrm{mol}^{-1}\mathrm{min}^{-1}$)	R^2
Avicel	0.0083	0.985	51	60	0.00019	0.986
Microfibrils	0.010	0.985	65	70	0.00035	0.992
Modified Avicel	0.0071	0.978	560	558	0.000029	0.981
Modified microfibrils	0.010	0.988	460	497	0.000031	0.992

influences adsorption of toluene in the modified fibres.

In this case also, the modified pure cellulose fibres have a higher retention capacity comparing with modified microfibrils for the same reasons mentioned above. The modified microfibrils adsorbed around 400 μmol of benzene and modified Avicel around 450 μmol of benzene per g of fibre.

In Fig. 9, the adsorption capacities of different modified fibres in a one compound solution are represented when the organic compound is toluene or benzene.

By comparing the retention capacity of modified fibres in a multicomponent solution with benzene and toluene, the amount of toluene absorbed is greater than the amount of benzene adsorbed in both modified cellulose fibres such as modified microfibrils and the retention speed is also higher in the case of toluene. This is consistent with data retention capacity of a single component where the toluene is adsorbed more and faster.

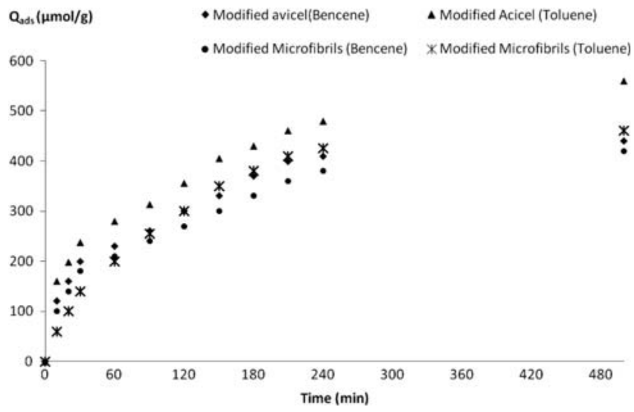

Fig. 9. Kinetic data of toluene or benzene adsorption onto different modified fibres.

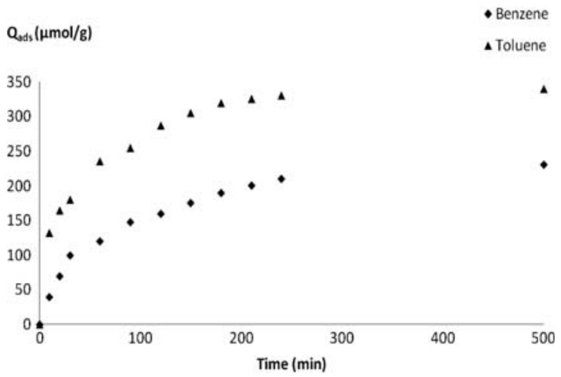

Fig. 10. Kinetic data of toluene and benzene adsorption onto modified Avicel.

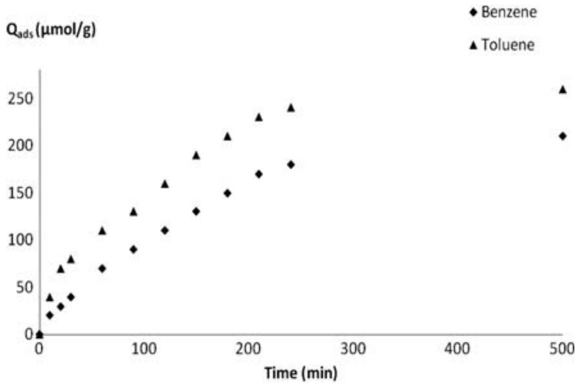

Fig. 11. Kinetic data of toluene and benzene adsorption onto modified microfibrils.

The retention capacities of modified Avicel are around 340 μmol of toluene per g of fibre and 230 μmol of benzene per g of fibre (Fig. 10). In the case of modified microfibrils, the retention capacities are around 260 μmol of toluene per g of fibre and 210 μmol of benzene per g of fibre (Fig. 11).

The retention capacities of each organic compound are lower when compared with the retention capacity of the fibres in a solution of a single component. But when we add the amount of adsorbed toluene and benzene, the modified fibres adsorbed almost the same amount as in a solution of a single component.

In the case of modified microfibrils, the retention capacity of benzene is similar to modified Avicel, but, this may be so because the amount of toluene adsorbed is less in the same time, so that the modified fibres are still able to adsorb therefore continue adsorbing benzene.

Moreover, this process also shows that the modified Avicel adsorbed more and faster than the modified microfibrils, as in the first part of this work, because microfibrils has non-cellulosic components.

4. Conclusion

The chemical processes used to obtain cellulose microfibrils were effective and have reduced considerably the non-cellulosic materials such as lignin. The TGA confirms that the treatment with palmitic acid improves the thermal stability of all samples. When the fibres are treated with palmitic acid, the hydrophobic character of pure cellulose samples and jute fibres resulted considerably increased as can be observed in contact angle values; this change of surface properties was more evident in the case of commercial microcrystalline cellulose (AVICEL), due to the availability of all hydroxyl groups are to react with palmitic acid. The adsorption capacity of modified cellulose varied with the aromatic compound used. Thus, the ability of modified cellulose to retain toluene is higher compared with benzene.

In a multicomponent solution, the ability of modified fibres to retain organic compounds does not vary significantly; the sum of the adsorption capacity is the same as for a single component solution.

In conclusion, the used chemical modification has increased significantly the adsorption capacity of native cellulose.

Acknowledgments

The research work was supported by the European Union and co-financed by the European Social Fund in the frame of the TAMOP-4.2.1/B-09/1/KONV-2010-0003 and TAMOP-4.2.2/B-10/1-2010-0025 projects, moreover by TAMOP-4.2.2-08/1/2008-0018, project entitled "Livable environment and healthier people—Bioinnovation and green technology research at University of Pannonia".

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