STUDY BY THERMAL METHODS ON THE MATERIALS OBTAINED BY DYE REMOVAL FROM WASTE WATERS WITH BEECH FLOUR

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The study is devoted to the characterization by both TG-DTG analysis and FTIR spectroscopy of beech flour, dyes and the sorbent-dyes products obtained through retention of the dyes from aqueous solution on the beech flour, to the aim of obtaining information on the nature of dyes' retention, thermal behavior of the sorbent-dye materials as well as on their possible upgrading as fuel.

Thermal analysis led to the conclusion that the mechanism of thermo-oxidative degradation is specific and the retention of dyes occurs on cellulose from beech flour. The nature of the bonds involved in dyes' retention is also investigated by FTIR analysis, which evidences that dyes retention on cellulose is realized through hydrogen bonding between the NH and, respectively, OH groups from dye molecule and the oxygen atoms from cellulose. Involvement of the non-participating electrons of the nitrogen and, respectively, oxygen atoms of these groups in the extended electronic conjugation with aromatic nuclei strongly influences the capacity of the amino and, respectively, hydroxyl groups of forming hydrogen bonds, thus achieving dyes fixation on the sorbent. DTA analysis led to the conclusion that an improvement in the quality of the sorbent-dye materials as fuels is possible, as compared to untreated beach flour, as a result of the modification of the cellulosic fibers in the process of dyes retention.

Keywords: *beech flour, DTA, DTG, dye removal, FTIR, TG, thermal analysis*

Introduction

In the recent years, the high amount of dyes used in dyeing processes at industrial scale, along with their increasingly diverse structure meant at meeting the equally increasing requirements of the market – have raised extremely important problem of growing concern at worldwide level, related to their efficient and complete elimination from residual waters [1, 2].

Although efficient, the classical methods of dye removal from waste waters have some drawbacks and are expensive [3]. As possible alternatives, several techniques have been proposed for the retention of dyes from waste waters on non-conventional, cheep and abundant sorbents, especially industrial (cellulosic and lignocellulosic) or agricultural (natural bio-polymers) residual products. Among such types of sorbents, special mention should be made of bamboo and jute fibers, sawdust [4–6], peat, moss, rice hull [7, 8], beech flour, modified lignin [9], coconut fiber [10], date tree stones [11], chitosane [12], eucalyptus bark [13]. Mineral clays (such as montmorillonites) have also been used as sorbents for organic dyes [14–17].

Following the studies devoted to the possible upgrading of the residual lignocellulosic products as sorbents [18–20], in a previous works [21] we analyzed the adsorption of some dyes frequently employed in textile industries from aqueous solution on beech flour, the optimum working conditions under which dyes retention is maximum being also settled.

The conclusion reached was that, out of the 9 dyes under test, beech flour shows maximum affinity towards: direct orange 8 (noted as C_1), direct brown 2 (C_4) and direct orange R (C_7). It has been also demonstrated that the retention of dyes from aqueous solution is much more efficient when using beech flour instead of other non-conventional lignocellulosic sorbents (spruce fir bark, oak flour).

The present study is devoted to the characterization, by non-isothermal thermal analysis methods and FTIR spectroscopy, of beech flour (F), of the dyes employed (C_1, C_4 and C_7) and of the sorbent-dye products (C_1F, C_4F and C_7F) obtained through the retention of dyes from aqueous solution on beech flour, to the purpose of obtaining information on the nature of dyes' retention, on the thermal behavior and stability of the sorbent-dye materials and also on their possible upgrading as a fuel.

Experimental

Materials

Beech flour as sorbent

The lignocellulosic material (beech flour) employed as a sorbent has been obtained from the wastes resulted from various industrial processing of beech wood. The particle diameter of the beech flour used in the present study (obtained through sieving) was of 0.315 mm.

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The C_1, C_4 and C_7 dyes

The dyes employed in the study of adsorption on beech flour [21], quite frequently used in textile industries, have the following structures (Scheme 1).

As beech flour evidences a more than ten times higher affinity for C_1, C_4 and C_7 than for the other dyes [21], the above-mentioned ones have been selected for studying the nature of the bonds involved in dye retention and thermal behaviour of the sorbent-dye materials.
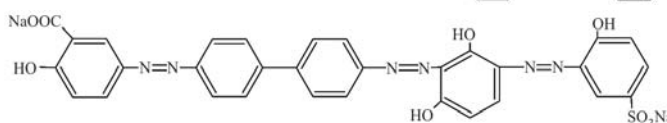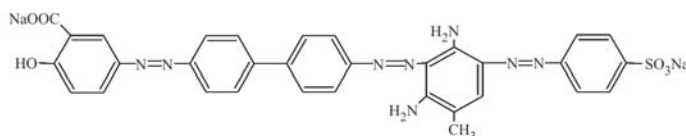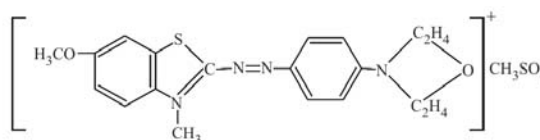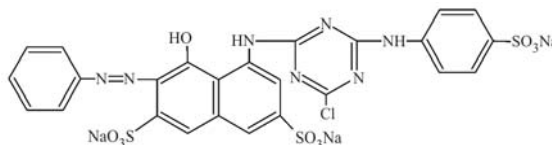
The C_1F, C_4F and C_7F materials

Adsorption of the C_1, C_4 and C_7 dyes on beech flour has been performed under the optimum conditions previously established as follows: concentration of the dye aqueous solution 700 µg mL^{-1} for C_1, 600 µg mL^{-1} for C_4 and, respectively, 900 µg mL^{-1} for C_7, temperature of 22°C, and the pH of the dye solution kept at 3 with acetic acid/acetate buffer. Under such conditions, the adsorption equilibrium was attained after 6 h for C_1 and, respectively, after 5 h, for C_4 and C_7.

Direct orange 8 (C_1)
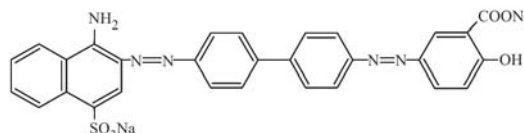
Direct blue 6 (C_2)
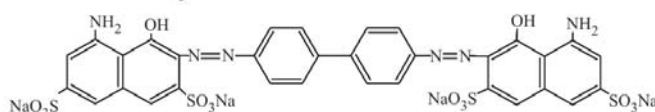
Direct orange 37 (C_3)
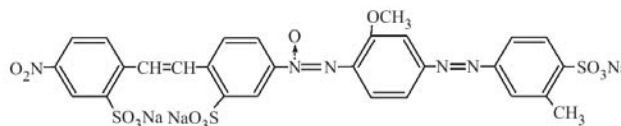
Direct brown 2 (C_4)
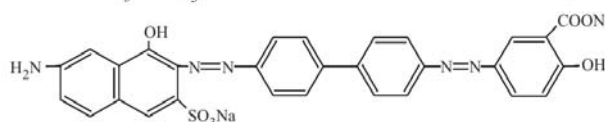
Direct green 26 (C_5)
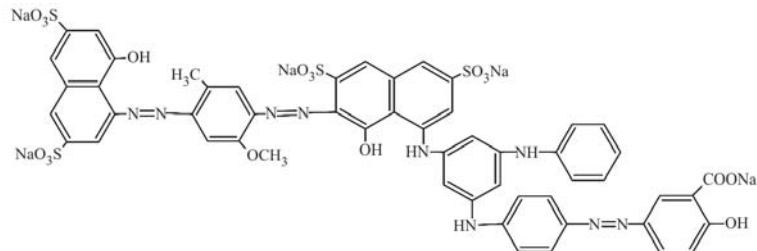
Direct brown 95 (C_6)

Direct orange R (C_7)

Basic blue 86 (C_8)

Reactive red (C_9)

Scheme 1

The C_1F, C_4F and C_7F materials have been separated from these systems through filtration, then dried at room temperature.

Methods

FTIR analysis

In this stage of the experiments, a Jasco FT-IR PLUS Spectrometer has been employed. The samples have been pelleted with KBr, and the transmittance spectra recorded over the 400–4000 cm^{-1} domain. All spectra recorded have been subsequently normalized to unity.

Thermal analysis

Thermogravimetric (TG, DTG) analysis have been performed on a Paulik–Paulik–Erdey type derivatograph (MOM, Hungary) with simultaneous recording of the T, TG, DTG and DTA curves. The working conditions are as follows: sample mass 100 mg, heating rate 10°C min^{-1}, maximum temperature 1000°C, DTG and DTA sensitivity 1/10, using freshly calcinated Al_2O_3 as reference material.

Results and discussion

Analysis of the TG and DTG curves of the samples under study leads to the conclusion that, as expected, a complex thermo-oxidative mechanism, possessing specific peculiarities, is involved.

Thermal degradation of the dyes takes place in several insufficiently separated stages. For illustration, the curve recorded for the C_4 dye is depicted in Fig. 1.

Table 1 lists the temperature values characteristic to the thermal degradation of the analyzed dyes.

Stage I is attributed to the elimination of the water from the samples (over the 28–194°C interval). The high complexity of the degradation mechanism does not permit separation of the subsequent stages (corresponding to thermo-oxidation processes), so
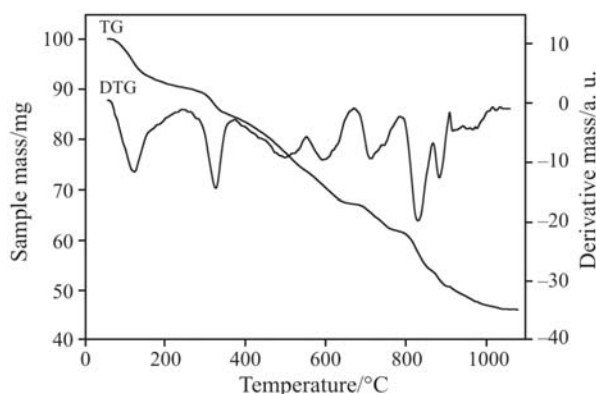

Fig. 1 TG and DTG curves for the C_4 dye

Table 1 Characteristic temperatures (°C) for the thermal degradation of the dyes

Sample	Stage I			Stage II
	T_i	T_m	T_f	T_i
C_1	28	80	130	229
C_4	71	129	194	283
C_7	40	97	135	245

T_i, T_m and T_f – initial, at the maximum degradation rate and final temperatures of the corresponding degradation stage.

only the initial degradation temperature could be determined [20, 22].

Beech flour and the C_1F, C_4F and C_7F materials are thermally degraded in three well-separated stages. Figure 2 plots the TG and DTG curves obtained for samples F, C_1F, C_4F and C_7F.

The characteristic temperatures of the degradation stages separated by TG-DTG analysis for samples F, C_1F, C_4F and C_7F, as well as the associated mass losses, are given in Table 2.

Stage I, proceeding over the 35–200°C interval, is attributed to the elimination of water from the samples. Both the characteristic temperatures and the corresponding mass losses (ranging between 5 and 9%) show that this process occurs in a similar manner in all

Table 2 Characteristic temperatures (°C), mass losses and residue for thermal degradation of samples F, C_1F, C_4F and C_7F

Sample	Stage I				Stage II								Stage III			Residue/%
					Peak I				Peak II							
	T_i	T_m	T_f	w_∞/%	T_i	T_m	T_f	w_∞/%	T_i	T_m	T_f	w_∞/%	T_i	T_f	w_∞/%	
F	35	96	200	8.8	210	344	369	27.0	269	400	450	28.0	455	809	35.7	0.5
C_1F	55	101	179	5.1	*211	330	345	21.2	368	380	430	14.6	430	783	39.4	2.0
					345	355	368	17.7								
C_4F	32	100	170	8.7	*185	316	324	20.3	358	–	407	10.9	407	782	42.1	1.3
					324	345	358	16.7								
C_7F	61	92	183	7.0	210	350	377	36.0	377	382	443	16.1	443	810	38.0	2.9

*the apparition of an inflexion point leads to the separation of two distinct processes
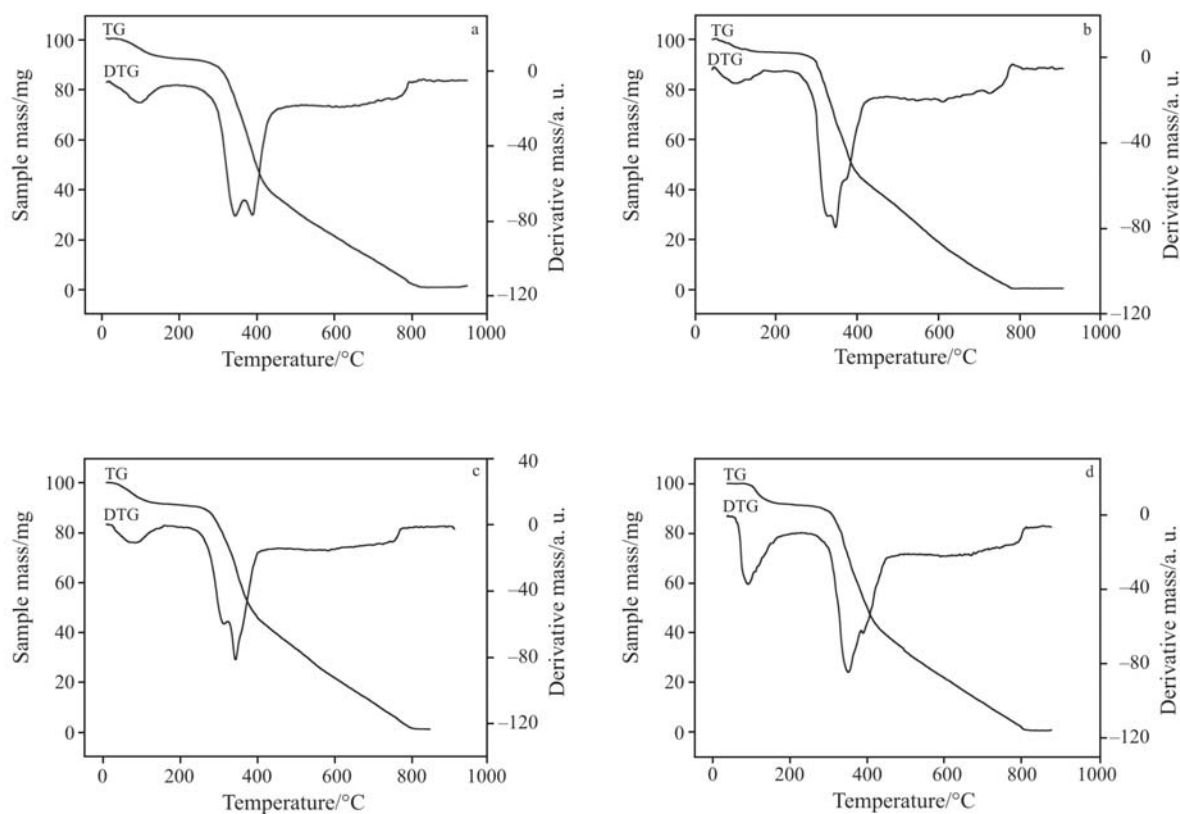
Fig. 2 TG and DTG curves for samples a – F, b – C_1F, c – C_4F and d – C_7F

samples subjected to analysis, dyes' retention having, from this point of view, no influence on the sorbent.

Stage II, proceeding over the 210–450°C interval and, respectively, stage III (between 407–810°C) correspond to samples thermo-oxidative degradation.

The characteristic temperatures of stage II indicate that over this interval both cellulose [23, 24] and the retained dyes are simultaneously degraded, their initial degradation temperatures being included in this interval. In the case of beech flour, two processes are separated in this stage, between 210–370°C and, respectively, 370–450°C, which may be explained by the co-existence of the low polymerization degree hemicellulose with the high polymerization degree cellulose, known as being thermally degraded within close temperature intervals [24].

The shape of the DTG curves in the second stage of degradation of C_1F, C_4F and C_7F samples is completely different from that plotted for beech flour (sample F), the modifications being caused by the presence of the retained dyes. In the case of C_1F and C_4F samples, two peaks are clearly separated within the 210–370°C temperature interval, which indicates the succession of two distinct degradation processes. The corresponding temperature intervals are: 211–345 and 345–368°C for C_1F and, respectively, 185–324 and 324–358°C for C_4F. With the C_7F sample, over the 210–377°C temperature interval, the DTG curve evi-

dences a single peak, the height of which is obviously superior to the one corresponding to sample F. Over the 368–430, 358–407 and, respectively, 377–443°C temperature intervals, samples C_1F, C_4F and, respectively, C_7F undergoes a degradation process similar to that identified for beech flour over the 369–450°C interval, attributed to the thermo-oxidative degradation of the high polymerization degree cellulose.

A comparative analysis of the mass losses corresponding to the processes separated in the second degradation stage evidences the different degradation behavior of samples C_1F, C_4F and C_7F comparatively with beech flour. For sample F, the mass losses corresponding to the two degradation processes attributed to the successive degradation of hemicellulose and, respectively of the high polymerization degree cellulose are 27 and 28%, respectively. In the case of sample C_1F, three degradation processes, with mass losses of 21.2, 17.7 and 14.6%, respectively, are separated, a situation similar to sample C_4F, for which the mass losses are of 20.3, 16.7 and 10.9%, respectively. In the case of C_7F sample, the mass losses occurring in the two degradation processes separated in this stage are of 36 and 16.1%, respectively.

All these observations lead to the conclusion that, over the 185–450°C temperature interval, corresponding to the second degradation stage, the influence of the dyes retained on the beech flour upon

thermo-oxidative degradation is manifested. In the case of samples C_1F, C_4F and C_7F, between 185–377°C are thermo-oxidatively degraded the hemicellulose, part of the high polymerization degree cellulose and the retained dyes. Later, up to 450°C, complete degradation of the high polymerization degree cellulose takes place. The shape of the DTG curves over the 185–450°C interval demonstrates a certain modification of the degradation mechanism of samples C_1F, C_4F and C_7F as compared to the sorbent.

The characteristic temperatures of the IIIrd stage of thermo-oxidative degradation indicates that over this temperature interval degradation of lignin takes place. The process occurs in a similar way in all 4 samples under analysis, suggesting that degradation of the retained dyes gets finalized in the second stage.

For getting additional information on the nature of dyes retention, a FTIR analysis of samples F, C_1F, C_4F and C_7F, as well as of the pure dyes (C_1, C_4 and C_7) has been performed. All spectra have been normalized to the unit, then the difference spectra (denoted as $C_1F–F$, $C_4F–F$ and $C_7F–F$) have been calculated through substraction of the normalized spectrum of beech flour (F) from those corresponding to samples C_1F, C_4F and respectively C_7F. The difference spectra thus obtained have been compared to those corresponding to pure dyes. For illustration purposes, Fig. 3 plots the FTIR spectra of samples F, C_1F and C_1, as well as the difference spectrum $C_1F–F$.
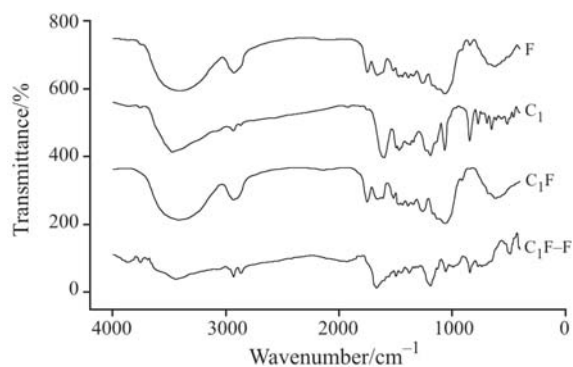

Fig. 3 FTIR spectra for samples F, C_1F, C_1 and the difference spectrum $C_1F–F$ (text)

The FTIR spectra of the dyes evidence absorption bands characteristic to the functional groups ($–NH_2$, $–OH$, $–SO_3Na$, $–COONa$, aromatic nuclei). The main absorption bands may be grouped as follows: the $–NH_2$ group evidences intense vibration bands in the 3300–3500 cm^{-1} region, and two intense deformation bands between 1590–1650 and 800–900 cm^{-1}, respectively; the phenolic group evidences vibration bands of the O–H bond between 3200–3500 and 800–900 cm^{-1} (which overlaps with the ones of the $–NH_2$ group), and intense vibra-

tion bands, characteristic to the C–OH bond, between 1030–1085 and 1180–1260 cm^{-1}. The $–SO_3Na$ group evidences an intense band between 1120–1230 cm^{-1}, while the bands characteristic to the carboxylate group are present between 1700–1780 cm^{-1} (the C=O bond) and respectively 1050–1120 cm^{-1} (the C–O bond). The C–H bonds show bands between 2800–3100 cm^{-1}, while the main bands characteristic to the aromatic nuclei appear between 1400–1500 and 800–900 cm^{-1} [25].

FTIR spectra of the C_1F, C_4F and C_7F samples evidence some modifications as compared to the F spectra, suggesting structural changes as an effect of dye retention on the cellulose. Consequently, a detailed analysis by comparison of the $C_1F–F$, $C_4F–F$ and $C_7F–F$ difference spectra with the spectra recorded for pure dyes have been performed.

A comparative analysis of the C_1 and $C_1F–F$ spectra, plotted in Fig. 3, puts into evidence certain modifications in the position and intensity of some significant bands. Thus, the intense band appearing at 1598 cm^{-1} in the C_1 spectrum, attributed to the N–H bond from the $–NH_2$ group, appears shifted at 1665 cm^{-1} in the $C_1F–F$ difference spectrum, with a 40% reduced intensity. Similarly, the intense band in the 3300–3500 cm^{-1} domain in the C_1 spectrum, where the vibration bands of the $–NH_2$ and $–OH$ groups are superposed, appears in the $C_1F–F$ spectrum with a 25% lower intensity and modified shape. The intense band from 1063 cm^{-1} in the C_1 spectrum, attributed to the C–OH bond, is only slightly shifted (1052 cm^{-1}) in the $C_1F–F$ spectrum and has an intensity reduced with 60%. The intense band from 845 cm^{-1} in the C_1 spectrum, also attributed to the $–NH_2$ group, may be observed in exactly the same position in the $C_1F–F$ spectrum, although with a 40% lower intensity. Analysis of the systems that include dyes C_4 and C_7 leads to identical results.

All these observations lead to the conclusion that dye fixation on cellulose is realized by hydrogen bonds between the $–NH_2$ and, respectively, $–OH$ groups from the dye molecule, and the oxygen atoms from cellulose. In the case of the C_1, C_4 and C_7 dyes, molecular structure favors conjugation of the non-participating electrons of the oxygen and, respectively, nitrogen atoms, from the $–OH$ and, respectively, $–NH_2$ groups, with the π electrons of the aromatic system, which reduces electronic density on such groups and facilitates the formation of hydrogen bonds. For the C_2, C_5, C_6 and C_9 dyes, the presence of substituents with electron-attracting effect ($–SO_3Na$ and $–COONa$) in meta position *vs.* the amino and, respectively, aromatic hydroxyl groups, negatively affects electronic conjugation of the non-participating electrons from the hydroxyl and, respectively, amino groups, while C_3

Table 3 Characteristic temperatures from DTA analysis and area of the exothermic peak

Sample	Stage I (endothermic)			Stage II (exothermic)		DTA peak area/a. u.
	$T_i/°C$	$T_m/°C$	$T_f/°C$	$T_i/°C$	$T_f/°C$	
F	45	101	200	200	811	3019
C_1F	82	118	180	180	785	3388
C_4F	37	100	170	170	781	3379
C_7F	63	112	183	183	810	3389

and C_8 do not possess either amino or hydroxyl groups. The absorption capacity of the beech flour for the latter six dyes was approximately 10 times lower than for C_1, C_4 and C_7, which indicates the important enhancing effect of the aforementioned extended electronic conjugation upon H bonding.

This conclusion could also explain the modification of the thermo-oxidative degradation mechanism of cellulose from the beech flour after dye retention, as the structure of the cellulosic fibers and, consequently, the fibers' behavior under heating could be affected by the hydrogen bonds formed.

DTA analysis provides some useful information for estimating the potential of the sorbent-dye materials obtained from the dye retention processes of being employed as fuel. To this purpose, DTA data obtained for these materials have been compared to those for untreated beech flour. The DTA curves corresponding to samples C_1F, C_4F, C_7F and to beech flour F, are depicted in Fig. 4.

For all samples, two distinct stages are observed in the DTA curve. The former stage, endothermic, is attributed to water elimination, as also evidenced by TG-DTG analyses. The latter, highly exothermic, corresponds to thermo-oxidative degradation. The high exothermicity of the process does not permit separation of the degradation processes on the DTA curve over this temperature interval. Table 3 lists the tem-

perature characteristic to the two stages and the area of the exothermic peak.

DTA peak area being a measure of the thermal effect of the corresponding process, the values listed in Table 3 demonstrate a pronounced increase of the thermo-oxidative thermal effect for samples C_1F, C_4F and C_7F as compared to untreated beech flour (sample F). This finding indicates some improvement in the quality of the woody material used as a fuel, attributed to the modification of the cellulosic fibers structure in the process of dye retention. A similar result has been attained when dyes had been retained on spruce fir bark [20], in which case the increasing effect of DTA peak area is much less pronounced, as a result of the much lower retention capacity of the spruce fir bark for such dyes.

Conclusions

TG-DTG analysis of the materials obtained by dye retention on beech flour led to the conclusion that the mechanism of thermo-oxidative degradation is a specific one. Dye retention occurs on the cellulose from the sorbent, modifying the mechanism of thermo-oxidative degradation of these materials as compared to untreated beech flour.

FTIR analysis supports the data of thermogravimetric analysis, leading to the conclusion that dye retention occurs by hydrogen bonding between the NH_2 and, respectively, OH groups from dye molecule, and the oxygen atoms from cellulose. The effect of the extended electronic conjugation involving the non-participating electrons of the nitrogen and, respectively, oxygen atoms of such groups on the capacity of forming hydrogen bonds, thus achieving dye fixation on the sorbent, is discussed.

DTA analysis evidences a certain improvement in the quality of the C_1F, C_4F and C_7F materials used as fuels, as compared to untreated beech flour, attributed to the modification of cellulosic fiber structure during dye retention.
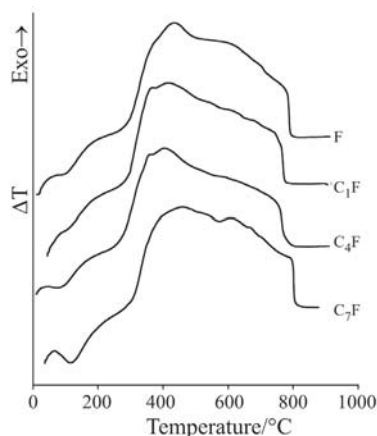
Fig. 4 DTA curves for samples F, C_1F, C_4F and C_7F

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