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The Biodegradabilities of Different Oil-Based Fatliquors

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Abstract The biodegradabilities of different oil-based fatliquors derived from rape oil, fish oil, castor oil or mineral oil variants were investigated by evaluating the respiration curves, BOD_5/COD values, COD (chemical oxygen demand) and TOC (total organic carbon) removal ratios. Simultaneously, degradation kinetics of the fatliquors were also studied. The results indicated that the BOD_5/COD values and the COD and TOC removal ratios of all the natural oil based products are higher than 0.45 and 85%, respectively, implying that all of them are biodegradable. The mineral oil based fatliquors have lower than 0.2 and 10% values, showing unbiodegradable characteristics and were used as the control. The biodegradability order is castor oil > fish oil > rape oil > mineral oil product. Further study indicated that the differences in biodegradability result from the varying fatty acid composition (such as ricinoleic acid and polyunsaturated fatty acids). The higher the active group content, the more beneficial for modification reactions and result in a higher biodegradation rate. The degradation kinetics studies revealed that the degradation rate constants (k) of castor oil, fish oil and rape oil products are 0.87, 0.84 and 0.81 d^{-1} for the sulfated fatliquor, and 0.95, 0.93, 0.85 d^{-1} for the oxidized–sulfited fatliquors, respectively; indicating that the overall degradation rate followed the same trend as the biodegradability order where castor oil > fish oil > rape oil, whether the fatliquors underwent modification as sulfated or oxidized–sulfited.

Keywords Biodegradability · Fatliquors · Oil · Fatty acid

Introduction

It is well known that the fossil raw materials are irrevocably decreasing and the pressure on the environment is building up. Thus the progressive trend that the chemical industry is turning to renewable raw materials, emerges as an inevitable necessity [1]. Natural oils have attracted renewed attention as raw materials for the preparation of various materials, to replace or augment the traditional petrochemical based materials. Triglycerides, which are composed of three fatty acids connected by a glycerol center, are the main component of natural oils, such as rape oil, fish oil and castor oil, etc. There are numerous ways of chemically modifying the unsaturated sites on the fatty acids and different applications in industry. In addition to their application in the food industry, triglyceride oils have been used for the production of coatings, inks, plasticizers, lubricants, agrochemicals, bitumen flux and leather fatliquors [2–4].

Fatliquoring is one of the key operations in the leather manufacturing [5]. It is an oil-addition process by which the leather fibers are lubricated so that after drying they are capable of slipping over one another and producing an adequate compliance and softness [6]. Natural oil (such as rape oil, fish oil and castor oil) and mineral oil based fatliquors are the two kind of widely applied products in the leather industry. Usually fatliquors are used in excess to ensure full penetration and complete reaction with leather fibers. As a result, unabsorbed fatliquors inevitably remain in the float, generating a high level of pollution. Moreover, it is the largest amount of chemicals (10–20 wt%, based on the weight of wet blue leather) used in the leather-making.

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The biodegradability of fatliquors is therefore considered as one of the most important factors associated in evaluating the environmental friendliness of a process in the leather industry.

Biodegradability of chemicals depends not only on the molecular structure of the tested compound but also on the availability of microorganism accessibility of metabolic cofactors (i.e., O_2, nutrients, etc.), growth medium and other environmental conditions, such as temperature and humidity [7]. However, the biomass, metabolic cofactors, growth medium and environmental conditions can be controlled with a standardized method. Therefore, the structure parameter, involving the main chain structure, substituted groups, polarity and active groups, is the key issue affecting the biodegradation. Knowing the relationship between the molecular structure and biodegradation of fatliquors could not only complement and substitute in part for some of the costly experimental evaluation of biodegradability but also help to identify and potentially avoid the production of new chemical compounds which are not easy to biodegrade. Thus, it would support the development of environmentally sustainable new products and the design of synthesis strategies if poorly degradable intermediates and waste products can be avoided [8, 9].

In our previous work, the rape oil was modified with different methods, such as sulfated, sulfonated, oxidized–sulfited, phosphated and copolymeric reactions. The effects of different modification methods on the biodegradability of rape oil-based fatliquors were investigated, and showed a biodegradability order of phosphated > sulfonated > oxidized–sulfited > sulfated > copolymeric [10]. The modification method which consumed the hydroxyl groups and double bonds, such as sulfated modification would decrease the biodegradability in 5 days. The others which did not consume those active groups, such as sulfonated and oxidized–sulfited, showed better biodegradability. In the polymerization method, the double bonds are consumed or modified, but due to the resulting larger molecular size and steric effect, the biodegradability is decreased [10]. In the current study, the different oils (rape, fish and castor oils) were modified uniformly (sulfated or oxidized–sulfited) and the difference in their biodegradabilities and degradation kinetics were investigated in detail by using mineral oil-based fatliquors (alkyl sulfonyl chloride) as a reference. The purpose of this study was to investigate how the structure parameters of the original oils influence the biodegradabilities of the modified products and to provide guidance for developing environmental-friendly fatliquors.

Experimental Procedures

Materials

Rape oil, fish oil and castor oil were obtained from Tingjiang Chemical Co. (Sichuan, China). All chemicals used for synthesis were of laboratory grade, while the chemicals used for analysis were of analytical grade.

Preparation of Different Oil-Based Fatliquors

The different oil-based fatliquors were prepared by sulfate and oxidized–sulfited reactions according to references [11, 12]. The reaction principles are shown in Fig. 1.

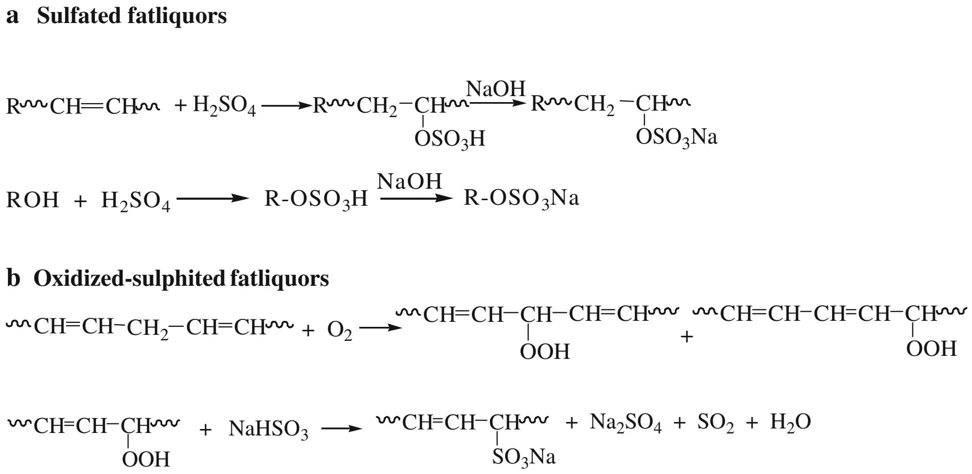
Characterizations

Fatty acid composition was determined by gas chromatography–mass spectrometry (GC–MS) (GC–MS TraceDSQII; ThermoFisher, USA) under the following conditions: oil transesterification to methyl esters; DB-5 capillary column 30 m × 0.25 mm i.d.; helium as carrier gas (40 kPa pressure); air pressure 100 kPa; hydrogen pressure 50 kPa; injection on column; flame-ionization detection at 220 °C and ionization energy of 70 eV; programmed oven temperature from 80 to 260 °C at 5 °C/min.

Iodine values were determined according to the ISO 3961 standard method. Whereas, the AOCS standard method Cd 13-60 was used to determine the hydroxyl values (expressed in mg of KOH per g of oil) [13].

Biodegradation was determined under aerobic conditions. Activated sludge from the aeration basin of a wastewater treatment plant was used as the microbial biomass for the test. Before use in the test, the sludge was washed twice with tap water and starved under aeration for 24 h. The concentration of the activated sludge was determined [14] and expressed as mixed liquid suspended solids (MLSS). The pH of the activated sludge was adjusted to 6.8–7.2 using a hydrochloric acid solution (1 M HCl) or a sodium hydroxide solution (1 M NaOH). In the test, the fatliquors were added to a mineral medium (Ingredients [15]: KH_2PO_4 1 g/L, KNO_3 0.5 g/L, $MgSO_4 \cdot 7H_2O$ 0.1 g/L, $CaCl_2$ 0.1 g/L, $FeCl_3$ 0.01 g/L, NaCl 1 g/L) as the sole source of carbon, and the sealed vessels with a headspace of air were inoculated with activated sludge (suspended solids 4 g/L). The tests were run for 5 days at 20 °C with continuous shaking. Biodegradation was monitored by plotting the biological respiration curve, BOD_5/COD value, as well as COD and TOC removal ratios.

Fig. 1 Preparation of different oil-based sulfated/oxidized–sulfited fatliquors (where *R* represents the rape oil, fish oil or castor oil based structure)



$$\mathrm{R{\sim}CH{=}CH{\sim}} + H_2SO_4 \longrightarrow \mathrm{R{\sim}CH_2{-}\underset{OSO_3H}{CH}{\sim}} \xrightarrow{NaOH} \mathrm{R{\sim}CH_2{-}\underset{OSO_3Na}{CH}{\sim}}$$

$$\mathrm{ROH} + H_2SO_4 \longrightarrow \mathrm{R{-}OSO_3H} \xrightarrow{NaOH} \mathrm{R{-}OSO_3Na}$$

$$\mathrm{{\sim}CH{=}CH{-}CH_2{-}CH{=}CH{\sim}} + O_2 \longrightarrow \mathrm{{\sim}CH{=}CH{-}\underset{OOH}{CH}{-}CH{=}CH{\sim}} + \mathrm{{\sim}CH{=}CH{-}CH{=}CH{-}\underset{OOH}{CH}{\sim}}$$

$$\mathrm{{\sim}CH{=}CH{-}\underset{OOH}{CH}{\sim}} + NaHSO_3 \longrightarrow \mathrm{{\sim}CH{=}CH{-}\underset{SO_3Na}{CH}{\sim}} + Na_2SO_4 + SO_2 + H_2O$$

The COD and BOD (biochemical oxygen demand) were measured by using Hanna HI 99721 and HI 99724A-6 equipment, respectively (Hanna Instruments, Italy). The data are averages of three separate measurements. The COD removal ratio is defined as:

$$\text{COD removal ratio }(\%) = (\text{COD}_0 - \text{COD}_5)/\ \text{COD}_0 \times 100$$

where COD_0 is the original chemical oxygen demand of the test sample solution (mg/L), and COD_5 is the chemical oxygen demand after the solution has biodegraded in 5 days.

TOC analyses were done using an Anatel TOC-2000 TOC analyzer (Shimadzu, Japan). The data are averages of three separate measurements. The TOC removal ratio is defined as:

$$\text{TOC removal ratio }(\%) = (\text{TOC}_0 -\ \text{TOC}_5)/\text{TOC}_0 \times 100$$

where TOC_0 is the initial and TOC_5 is the final chemical oxygen demand of the test sample solution (mg/L) after biodegradation in 5 days.

Results and Discussion

Analysis of Fatty Acid Composition of the Oils

Rape oil, castor oil and fish oil are typical natural renewable oils, and mineral oil is a representative of non-renewable fossil oil and are widely used in the leather industry as fatliquors. Rape oil, castor oil or fish oil based sulfated or oxidized–sulfited fatliquors, as well as the alkyl sulfonyl chloride fatliquors are frequently used natural or mineral oil based fatliquors, respectively. The fatty acid composition (summarized in Table 1) differ in each oil sample. Table 2 lists the statistical saturated, monounsaturated and

Table 1 The fatty acid composition of the oils

Fatty acid	Molecular formula (number of double bonds)	Composition (wt%)
Rape oil		
Palmitic acid	$C_{16}H_{32}O_2$ (0)	16.2
Heptadecanoic acid	$C_{17}H_{32}O_2$ (1)	0.9
Linolenic acid	$C_{18}H_{30}O_2$ (3)	2.7
Linoleic acid	$C_{18}H_{32}O_2$ (2)	15.2
Oleic acid	$C_{18}H_{34}O_2$ (1)	54.2
Stearic acid	$C_{18}H_{36}O_2$ (0)	6.3
Gadoleic acid	$C_{20}H_{38}O_2$ (1)	2.6
Arachidic acid	$C_{20}H_{40}O_2$ (0)	1.2
Fish oil		
Myristic acid	$C_{14}H_{28}O_2$ (0)	5.6
Palmitoleic acid	$C_{16}H_{30}O_2$ (1)	7.8
Palmitic acid	$C_{16}H_{32}O_2$ (0)	15.4
Margaric acid	$C_{17}H_{34}O_2$ (0)	3.2
Stearic acid	$C_{18}H_{36}O_2$ (0)	4.6
Oleic acid	$C_{18}H_{34}O_2$ (1)	13.9
Gadoleic acid	$C_{20}H_{38}O_2$ (1)	7.1
5,8,11,14,17-Eicosapentaenoic acid (EPA)	$C_{20}H_{30}O_2$ (5)	14.7
Heneicosapentanoic acid	$C_{21}H_{32}O_2$ (5)	5.4
Erucic acid	$C_{22}H_{42}O_2$ (1)	9.4
Docosahexaenoic acid (DHA)	$C_{22}H_{32}O_2$ (6)	12.9
Castor oil		
Palmitic acid	$C_{16}H_{32}O_2$ (0)	2.3
Margaric acid	$C_{17}H_{34}O_2$ (0)	8.1
Stearic acid	$C_{18}H_{36}O_2$ (0)	2.2
Oleic acid	$C_{18}H_{34}O_2$ (1)	0.7
Linoleic acid	$C_{18}H_{32}O_2$ (2)	7.5
Ricinoleic acid	$C_{18}H_{34}O_3$ (1)	79.2
Mineral oil		
Saturated hydrocarbons	C_nH_{2n+2} (n = 11–24)	98.4

Table 2 The statistic saturated, monounsaturated and polyunsaturated composition contents for different oils (%)

Oil	Saturated	Monounsaturated	Polyunsaturated
Rape oil	24.7	59.3	18.0
Fish oil	27.8	39.2	33.0
Castor oil	12.6	79.9	7.5
Mineral oil	98.4	1.6	–

polyunsaturated fatty acids components. As shown in Tables 1, 2, castor oil, with huge amount of ricinoleic acid, has the lowest amount of saturated fatty acids. The ricinoleic acid (Fig. 2) contains hydroxyl group on the molecular backbone which is not present in other oil. The polyunsaturated fatty acids [in the form of EPA, DHA and heneicosapentanoic acid (Fig. 2)] composition in fish oil is about 33%. The monounsaturated fatty acids in rape oil are the majority and polyunsaturated fatty acids existed only in the form of biunsaturated or triunsaturated fatty acids. The mineral oil is composed primarily of saturated hydrocarbon, with minor double bonds and no hydroxyl groups.

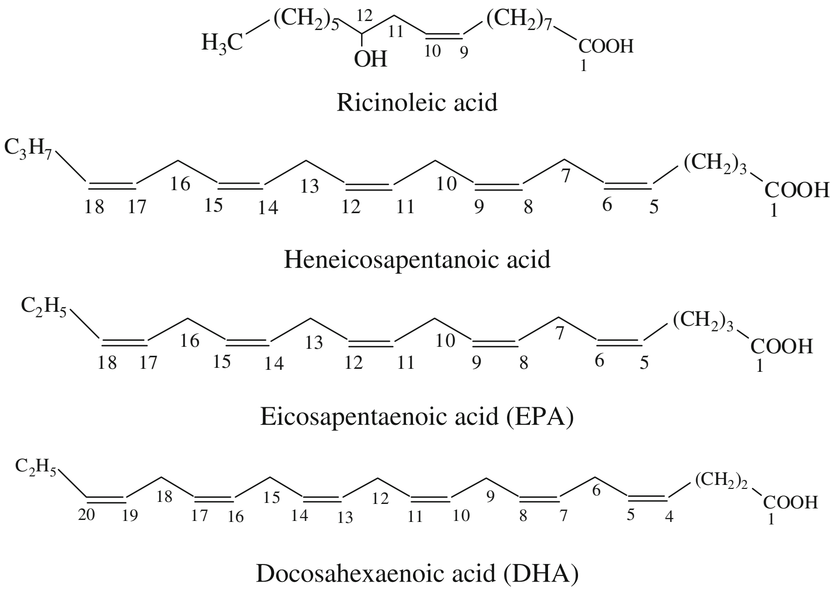
The Biodegradabilities of Different Oil-Based Sulfated Fatliquors

The activated sludge process is an efficient and widely used method in wastewater treatment [16]. Respiration is the essential activity of aerobic microorganisms in the activated sludge. The respiration of the activated sludge will be different from its endogenous respiration when there are chemicals in wastewater. Thus, the biodegradability of the fatliquors can be qualitatively evaluated by the difference in biological respiration curves [17] (the respiration curve is the curve that the BOD change with time). When a biodegradable chemical is utilized as a carbon and energy source for the organism growth in activated sludge, the respiration of activated sludge will be enhanced; In contrast, if the chemical is toxic to the microorganisms of the activated sludge, the respiration will be inhibited. The respiration curves of rape oil, fish oil, castor oil based sulfated fatliquors and mineral oil-based fatliquors (alkyl sulfonyl chloride) as well as the endogenous respiration curve of the activated sludge are shown in Fig. 3.

The respiration curves of activated sludge in the presence of the three natural oil-based fatliquors individually, are all above the endogenous respiration curve, which means that all of them are biodegradable. And the respiration curve of activated sludge in the presence of castor oil based fatliquors is higher than fish and rape oil indicating that the biodegradability of the castor oil type fatliquors is the best, and the biodegradability of rape oil based fatliquors is not as good as other two. However, the respiration curve of the alkyl sulfonyl chloride is lower than the endogenous respiration curve, suggesting that the mineral oil based fatliquors could not be biodegraded by the activated sludge.

The biodegradability of an organic compound can also be evaluated by measuring the BOD_5/COD values. The BOD_5 is the amount of oxygen consumed by biochemical oxidation of waste contaminants over a 5-day period. A higher BOD_5/COD ratio is associated with better biodegradability [18]. A compound is usually considered as an easily biodegradable one when its BOD_5/COD value is higher than 0.45. On the contrary, it is considered as a hardly biodegradable one when the value is lower than 0.20

Fig. 2 Molecular structures of ricinoleic acid and polyunsaturated fatty acids



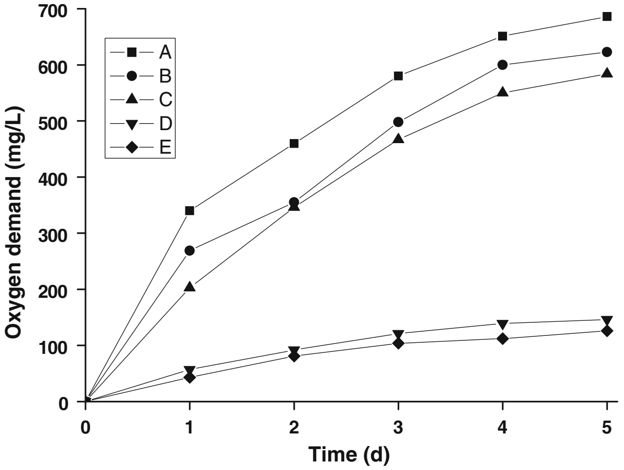


Fig. 3 The respiration curves of activated sludge in presence of different oil-based sulfated fatliquors [**a** castor oil, **b** fish oil, **c** rape oil, **d** the respiration curves of activated sludge, **e** mineral oil (alkyl sulfonyl chloride)]

[18]. In Table 3, the BOD_5/COD value is shown to be greater for castor oil based fatliquors than for other natural oil-based fatliquors but all have higher than 0.45 values. Whereas the alkyl sulfonyl chloride's is lower than 0.2 ratio, indicating that all natural oil-based fatliquors are biodegradable, while the mineral oil fatliquors are not.

The biodegradability of chemicals determined by activated sludge respiration is based on the oxygen consumption of aerobic microorganisms. The oxygen consumption is characterized by the COD value and is commonly used as a crucial parameter to reflect total pollution content in the wastewater. However, due to the physical adsorption of the activated sludge to the chemicals, the COD value cannot solely reflect the biodegradation. Thus, biodegradation is further confirmed by the TOC removal ratio analysis. When the soluble carbon of the biodegradable chemicals in the wastewater is utilized as the source of carbon and energy for the growth of organisms in activated sludge, [19] it is gradually consumed by the organisms, resulting in a decrease of the TOC value after treating with activated sludge for 5 days.

As shown in Table 3, the TOC removal ratios of all the natural oil based fatliquors are higher than 85%, but the mineral oil fatliquors is lower than 10%, which is in agreement with the order of the COD removal ratios.

The difference in the biodegradabilities of these fatliquors can be attributed to different fatty acid composition and active groups' content after modification. As mentioned in Fig. 1, the sulfated reaction mainly consumed double bonds and hydroxyl groups, so after modification the hydroxyl and iodine values were decreased for all samples as shown in Table 4. For castor oil the hydroxyl value is higher than the others while the iodine value is almost the same as the other products after modification. It is believed that due to their electron donating capability, the hydroxyl groups have played an important role in castor oil biodegradation.

For fish oil and rape oil based fatliquors, it is the double bond content that dominantly influence their biodegradation rather than the hydroxyl groups' content. The iodine value in fish oil is higher than the rape oil, but after modification, the iodine values are almost the same in all oil samples. This can be attributed to the polyunsaturated fatty acids [such as EPA, DHA and heneicosapentanoic acid, see Fig. 3] content in the oils, the former is greater for the latter, and these non-conjugated double bonds are beneficial for both modification reactions and faster biodegradation. In rape oil, the double bonds existed mainly in the monounsaturated fatty acids, and the activity of these double bonds is less than the non-conjugated double bonds, hence the biodegradation by cleavage the double bond is

Table 3 BOD_5/COD values and COD, TOC removal ratios of different oil-based sulfated or oxidized–sulfited fatliquors in 5 days of biodegradation

Fatliquors	BOD_5/COD	COD_0 (mg/L)	COD_5 (mg/L)	COD removal (%)	TOC_0 (mg/L)	TOC_5 (mg/L)	TOC removal (%)
–Alkyl sulfonyl chloride	–	558	530	4.98	553	525	5.02
Castor oil							
Sulfated	0.97	557	5	99.1	661	5	99.2
Oxidized–sulfited	0.98	561	4	99.3	674	3	99.5
Fish oil							
Sulfated	0.92	519	12	97.7	541	9	98.3
Oxidized–sulfited	0.95	525	10	98.1	559	6	98.9
Rape oil							
Sulfated	0.87	500	50	90.0	527	36	93.2
Oxidized–sulfited	0.93	510	33	93.5	543	26	95.2

– BOD_5 undetectable

Table 4 The iodine and hydroxyl values of the fatliquors before and after modification

	Oil		
	Castor oil	Fish oil	Rape oil
Iodine value (gI/100 g)			
Before modification	85	176	106
Sulfate modification	41	49	42
Oxidized-sulfite modification	72	152	84
Hydroxyl value (mg KOH/g)			
Before modification	170	10	11
Sulfate modification	55	5	7
Oxidized-sulfite modification	165	8	9

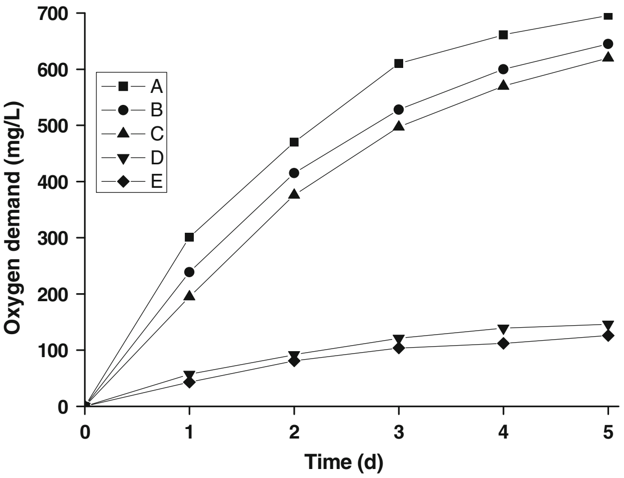


Fig. 4 The respiration curves of activated sludge in presence of different oil-based oxidized–sulfited fatliquors (**a** castor oil, **b** fish oil, **c** rape oil, **d** is the respiration curves of activated sludge), **e** alkyl sulfonyl chloride (mineral oil)

slower than the polyunsaturated fatty acids; that is why the biodegradability of rape based fatliquors is inferior to the other two products.

However, in the mineral oil fatliquors, the major components are saturated hydrocarbon derivatives and no hydroxyl groups or double bonds are involved. The long chain alkyl groups (long C–C chains) are quite difficult to biodegrade, and the existence of the strong electron-withdrawing group (–Cl) further decrease its biodegradability.

The Biodegradabilities of Oxidized–Sulfited Fatliquors

Figure 4 displays the respiration curves of the oxidized–sulfited fatliquors and mineral oil based fatliquors, as well as the endogenous respiration curve of the activated sludge. It can be seen that the substrate respiratory curves of the natural oil fatliquors are all above the endogenous respiration curve, showing good biodegradabilities. On the contrary, the respiratory curves in presence of alkyl sulfonyl chloride is below the endogenous respiration curve which means the alkyl sulfonyl chloride can hardly be degraded by the microorganism.

Similar conclusions can be drawn from the analysis of BOD_5/COD values, COD and TOC removal ratios. As shown in Table 3, the natural oil based oxidized–sulfited fatliquors are easily degraded whilst the mineral oil based fatliquors is hardly degraded. As shown in Table 4, the changes tendency of hydroxyl and iodine values for all oxidized–sulfited samples are the same for the sulfated fatliquors, so the biodegradability show the same order.

The Biodegradation Kinetics of Different Oil Based Fatliquors

The respirations, BOD_5/COD values and COD, TOC removal ratios analysis can provide a possibility of biodegradation but cannot tell which one biodegrade faster or slower. Previous studies indicated that the BOD with time of low concentration organic compound under activated sludge treatment, approached to single-molecule reaction mechanism, and accorded with first-order reaction kinetics model [20].

Respiration rate is the oxygen consuming rate of the aerobic microorganisms that participate in the biodegradation. Assume that the ultimate BOD is L_0 (the total amount of oxygen consumed when the biochemical reaction is allowed to proceed to completion is called the ultimate BOD), and then at time t (d) the respiration rate is proportional to the residual BOD L_t, and can be derived as Eqs. (1)–(3):

$$\frac{dL_t}{dt} = -kL_t \tag{1}$$

$$L_t = L_0 \exp[-k(t - t_0)] \tag{2}$$

Thus,

$$y_t = L_0 - L_0 \exp[-k(t - t_0)] \tag{3}$$

where, L_0 represents the ultimate BOD (mg/L), and residual BOD L_t is the total remaining BOD at time t (mg/L), that is subtracting the BOD of time t from ultimate BOD; y_t is the BOD at time t (mg/L); k is the rate constant of BOD (1/d); t_0 is persists time (d).

This model contains three kinetics parameters which reflect the different biodegradabilities of these fatliquors. L_0/COD is the direct reflection of the degree of degradation; k describes degradation rate (the larger the k value is, the quicker the biodegradation reaction will be) and t_0 reflects the adaptability of the activated sludge with fatliquors, t_0 means the time when the biodegradation reaction start. The values for the model parameters after model optimization are shown in Table 5.

Table 5 Model parameter values for the fatliquors

	COD (mg/L)	t_0 (h)	k (1/d)	L_0 (mg/L)	Biodegradation (%)
Castor oil					
Sulfated	557	1.54	0.87	549	98.5
Oxidized–sulfited	561	1.04	0.95	557	99.3
Fish oil					
Sulfated	519	2.14	0.84	486	93.7
Oxidized–sulfited	525	1.35	0.93	507	96.5
Rape oil					
Sulfated	500	2.43	0.81	446	89.2
Oxidized–sulfited	510	2.39	0.85	479	93.9

The degradation rate or *k* values of the tested fatliquors, either sulfated or oxidized–sulfited products, show a uniform order that castor oil > fish oil > rape oil. Biodegradation kinetics study also confirms the above conclusion, that is, the biodegradability of different oil-based fatliquors are mostly associated with the fatty acid composition and active groups (double bonds and hydroxyl groups) content in the oils, higher contents of them are beneficial for their biodegradation.

Conclusions

1. These cumulative results indicate that the fatty acid composition is the most important factor associated with the biodegradabilities of different oil-based fatliquors. The presence of hydroxyl groups containing a fatty acid (ricinoleic acid) and non-conjugated polyunsaturated fatty acids, such as EPA, DHA and heneicosapentanoic acid are essential for both modification reactions and faster biodegradation.
2. The active group content depends on the fatty acid composition. The fatty acid composition and the amount of the active groups such as the double bonds and hydroxyl groups can directly affect the biodegradabilities of these fatliquors. The higher the content of unsaturated fatty acids and hydroxyl groups, the faster is the biodegradability of fatliquors.
3. The biodegradability of natural oil based fatliquors is superior to mineral type, and generating the order of castor oil > fish oil > rape oil > mineral oil.
4. The overall degradation rate or k values of the tested fatliquors, either sulfated or oxidized–sulfited products, followed the same trend as the biodegradability order.

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