The Biodegradabilities of Rape Oil-Based Fatliquors Prepared from Different Methods

by

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Abstract

Rape oil-based fatliquors were prepared from different methods such as sulfated, sulfonated, oxidized-sulphited, phosphated or copolymerization and their biodegradabilities were investigated by evaluations of the respirations, BOD_5/COD values and COD, TOC removal ratios. The results indicate that the BOD_5/COD values and the COD, TOC removal ratio of all products are higher than 0.45 and 85%, respectively, showing a biodegradability order of phosphated > sulfonated > oxidized-sulphited > sulfated > copolymeric and biodegradable characteristics. Further study indicates that the difference in the biodegradability is closely related to the content of double bonds and hydroxyl groups in resultant fatliquors for different modification methods; the one which consumes the double bonds or hydroxyl groups will decrease its biodegradability, whilst others which do not consume the double bonds or hydroxyl groups will impart the product better biodegradability.

Resumen

Engrasantes basados en aceite de colza fueron preparados por diferentes métodos de síntesis; las variantes incluyendo sulfatados, sulfonados, sulfitados-oxidados, fosfatados y copolimerizados. Su biodegradabilidad fue investigada por las evaluaciones de respiración, los valores de DBO_5/DOC y DOC, las tasas de eliminación de TOC. Los resultados indican que los valores de DBO_5/DOC y DOC y las tasas de eliminación de TOC de todos los productos son más altas, 0,45 y 85% respectivamente, revelando un orden en la característica de biodegradabilidad de fosfatado > sulfonado > sulfitado-oxidado > sulfatado > copolimerizado. Otros estudios indicaron que las diferencias en la biodegradabilidad estaban estrechamente relacionadas con el contenido de los dobles enlaces y los grupos hidroxilo en los engrases preparados por los diferentes métodos de modificación. Los métodos que consumen los dobles enlaces o grupos hidroxilo mostraron disminución en la biodegradabilidad, mientras que otros que no consumen los dobles enlaces o grupos hidroxilo han dado lugar a productos con una mejor biodegradabilidad.

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INTRODUCTION

The concept of cleaner production has a great importance nowadays. The exhaustion of resources and the high pollution level increase the need for alternative methods that can minimize waste and maximize biodegradation of waste.[1] An alternative process is designed to use environmental-friendly material that is easy to biodegrade in the environment. In fact the use of biodegradable chemicals is also reasonable in economics terms since a lower cost of wastewater treatment is needed to meet discharge standards. Thus the estimation of biodegradation of leather chemicals is an important source in chemical environmental friendliness assessment. Prediction of the biodegradability of organic compounds is an ecologically desirable and economically feasible tool for estimating the environmental fates of chemicals. Knowing the biodegradation of leather chemicals enables tanners to select chemicals with consideration of both quality insurance and environmental friendliness. In order to produce soft leather, after retanning it is processed through a fatliquoring step, which has the objective to treat the collagen fiber with oil, thereby lubricating them, and make the leather soft and have a pleasant feel.[2] It is a very important step to confer the final mechanical, aesthetic and handle characteristics of leather.[3] The fatliquoring operation is designed to introduce oils and fats into the leather matrix in finely dispersed form in a water medium.[4] This is achieved by emulsification processes through the introduction of hydrophilic groups, such as sulfate, sulfonate, sulfite or phosphate groups into the structure of oils and fats or by addition of surfactants to the composition of fatliquors. Usually fatliquors need to be used in excess to ensure full penetration and complete reaction between fatliquors and leather fiber. As a result, a part of the fatliquors employed would inevitably remain in the float, leading to a high level of pollution emission. Moreover, fatliquors are the largest amount of chemicals (10-20wt% on wet blue) used in the leather-making. Thus the biodegradability of fatliquors is one of the most important factors associated with environmental friendliness of leather industry. Biodegradability depends not only on the molecular structure of the tested compound but also on the microorganisms available and on other environmental conditions, such as temperature and humidity.[5] However, the biomass and environmental conditions can be controlled with a standardized method. Thus the molecular structure (substituted groups, polarity active groups, et al.) is the most important issue associated with the biodegradation. Depending upon the source of the oils/fats used, the fatliquors can be classified as natural, synthetic and semi synthetic. Generally, synthetic fatliquors (e.g. chlorinated paraffin) are difficult to biodegrade, because their long chain alkyl groups (long C-C chains) are quite difficult to be cleaved by biodegradation. Among the natural types, rape oil-based fatliquors is one of the most important fatliquors and it is widely used in leather fatliquoring, because rape oil with higher level of erucic acid (*cis*-13-docosenoic acid) is more available in China and the erucic acid has good hydrophobic properties and lubricating ability.[6] Knowing the relationship between the modification method 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 biodegradable. Thus, it would support the development of environmentally sustainable new products and the design of synthesis strategies that avoid poorly degradable intermediates and waste products.[7-8]

Up to now, there is no research on the relationship between the modification method and biodegradation of fatliquors, although some research concerning the biodegradation of leather chemicals has been published.[9] Sun D.H. and He Q., et al., evaluated the environmental impact of typical leather chemicals, such as fatliquors, organic tanning agents and retanning agents.[10-12] However they mainly focus on the evaluation methods, not the relationship between the structure of leather chemicals and biodegradation. In an attempt to explore the influence of structure parameters which are closely related to the modification method on the biodegradability of rape oil-based fatliquors, in this study, the biodegradabilities of rape oil-based fatliquors of different modified methods derived from sulfated, sulfonated, oxidized-sulphited, phosphated or copolymeric variants were investigated.

EXPERIMENTS

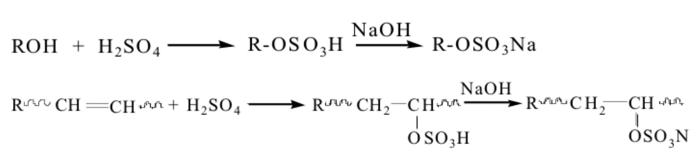
Materials

Rape oil (Iodine value is 108 gI/100g) were obtained from Tingjiang Chemical Co. (Sichuan, China). All chemicals used for synthesizing were of laboratory grade, while the chemicals used for the analysis were of analytical grade.

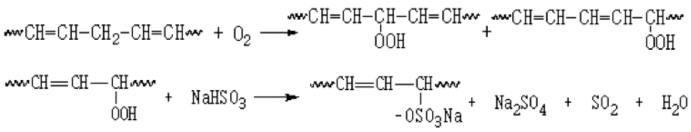
Preparation of rape oil-based fatliquors

The synthesis methods of sulfated, sulfonated, oxidized-sulphited and phosphated rape oil were according to the reference.[13-16] Firstly, rape oil was reacted with 1 to 1.5 equivalents of methanol at 60-65 °C for 4h to obtained partial ester exchange rape oil (transesterification), and then it was sulfated, sulfonated, oxidized-sulphited and phosphated, respectively. The copolymeric rape oil-based fatliquors was prepared by the reference method.[6] The reaction principles are shown in figure 1.

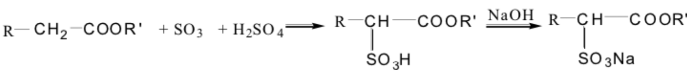
a. Sulfated rape oil



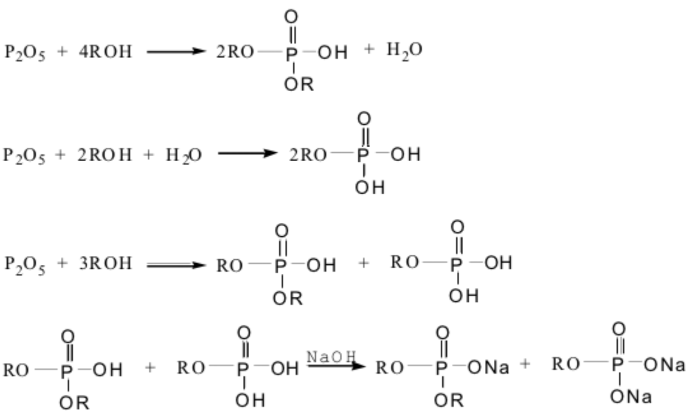
b. Oxidized-sulphited rape oil



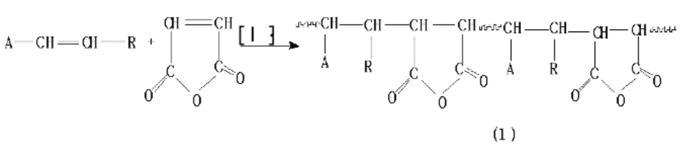
c. Sulfonated rape oil



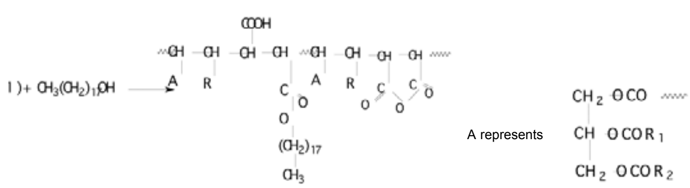
d. Phosphated rape oil



e. Copolymeric rape oil-based fatliquors



Step 1 Free radical copolymerization between maleic anhydride and rape oil



Step 2 Esterification with octadecyl alcohol

Figure 1. – Preparation of rape oil-based fatliquors (where R represents the oil based structure and R' is the long chain fatty acid structure.)

Characterizations

Iodine number and hydroxyl value were determined according to the ISO 3961 standard and AOCS standard methods Cd 13-60, respectively.[17] The hydroxyl value is expressed in mg of KOH per g of oil. Biodegradation is determined under aerobic conditions. In the test the fatliquors were added to a mineral medium (Ingredient: KH_2PO_4 1g/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 diluted fresh activated sludge from a wastewater treatment plant in Chengdu (suspended solids 4 g/L). The tests were run for 5 days at 20 °C with continuous shaking. Biodegradation is monitored by biological respiration curve, BOD_5/COD value, COD (chemical oxygen demand) and TOC (total organic carbon) removal ratios.

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:

$$\text{COD removal ratio (\%)} = (COD_0 - COD_5)/\ COD_0 \times 100\%$$

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 been biodegraded for 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:

$$\text{TOC removal ratio (\%)} = (TOC_0 - TOC_5)/\ TOC_0 \times 100\%$$

Where TOC_0 is the original chemical oxygen demand of the test sample solution (mg/L), and TOC_5 is the chemical oxygen demand after the solution has been biodegraded for 5 days.

RESULTS AND DISCUSSION

Relationships among the respiration, BOD_5/COD value, COD, TOC removal ratios and biodegradation

The activated sludge process is an efficient and widely used method in wastewater treatment.[18] Respiration is the essential activity of aerobic microorganisms in the activated sludge. The respiration of activated sludge will be different from its endogenous respiration when there are chemicals in wastewater. When a biodegradable chemical is utilized as the source of carbon and the energy for the growth of the organisms in activated sludge, the respiration of activated sludge will be enhanced. On the contrary, if the chemical is toxic to the microorganisms of the activated sludge, the respiration will be inhibited. Thus, the biodegradability of the fatliquors can be qualitatively evaluated by comparing the difference in biological respiration curves.[19] The

TABLE I

The relationship between BOD_5/COD value and the biodegradability of the organic compound

BOD_5/COD	>0.45	0.3~0.45	0.2~0.3	<0.2
Biodegradability	easier	easy	difficult	hardly biodegrade

TABLE II

The iodine values and hydroxyl values of the resultant fatliquors

Values		Methods				
		copolymeric	sulfated	oxidized-sulphited	sulfonated	phosphated
iodine value (gI/100g)	before modification	106	106	106	106	106
	after modification	36	42	85	102	104
hydroxyl value (mgKOH/g)	before modification	—	141	141	141	141
	after modification	—	25	130	136	17

("—" means very low to negligible.)

TABLE III

BOD_5/COD values and COD, TOC removal ratios of rape oil-based fatliquors in 5 days of biodegradation

Rapeseed oil	BOD_5/COD	COD_0 (mg/L)	COD_5 (mg/L)	COD removal (%)	TOC_0 (mg/L)	TOC_5 (mg/L)	TOC removal (%)
phosphated	1.0	508.3	17.8	96.5	535.6	7.0	98.7
sulfonated	0.95	526.3	26.8	94.9	564.3	16.4	97.1
oxidized-sulphited	0.93	510.4	32.7	93.6	543.2	25.5	95.3
sulfated	0.87	500.2	50.0	90.0	527.0	35.8	93.2
copolymeric	0.69	518.8	70.1	86.3	553.2	58.6	89.4

biodegradability of a chemical could also be evaluated by the value of BOD_5/COD, which is a simple method to evaluate the biodegradability of organic compounds in environment engineering. A higher BOD_5/COD ratio is associated with a better biodegradability.[20] The relationship between BOD_5/COD value and the biodegradability of the organic compound are shown in Table I.[21] If the BOD_5/COD value of a chemical is higher than 0.45, it is easily biodegradable.

The biodegradability of chemicals determined by activated sludge respiration is based on oxygen consumption of aerobic microorganisms. The oxygen consumption is characterized by COD value and it is commonly used as a crucial parameter to reflect total content of pollutions in the wastewater. Therefore, the degree of COD removal ratio of a chemical after treating with activated sludge for 5 days is able to characterize the efficiency of biological treatment process and the biodegradability of the fatliquors. However, due to the physical adsorption of the activated sludge to the chemicals, the COD value cannot solely reflect the biodegradation. Thus, the biodegradation should be 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,[22] it will be gradually consumed by the organisms, resulting in the decrease of the TOC value. So the biodegradability of a chemical can also be characterized by the degree of TOC removal after treating with activated sludge for 5 days.

The biodegradabilities of the fatliquors under activated sludge can be characterized by biological respiration curves, BOD_5/COD value, COD and TOC removal ratios. And the biodegradability depends on the modification methods and the active groups available in the fatliquors.

The influence of modification methods on the active groups of fatliquors

As already known, the polar groups in chemicals affect their biodegradability; a higher content of polar groups (such as –COOH, -COO-, -OH, double bonds) is beneficial for their biodegradation.[23] In modification process, some polar groups were introduced on the oil molecule and simultaneously some active groups were consumed, so the biodegradabilities of these fatliquors are different from each other. To explore the influence of active groups on the biodegradabilities of fatliquors, the changes of typical active groups (double bonds and hydroxyl groups) with different modification methods were studied. In analytical chemistry, the content of double bonds and hydroxyl groups in the fatliquors can be characterized by the iodine value and hydroxyl value, separately, and the higher the iodine value or hydroxyl value is, the more double bonds or hydroxyl groups are present in the fatliquors per unit mass. As illustrated in Table II, the iodine values of sulfated and copolymeric fatliquors decrease

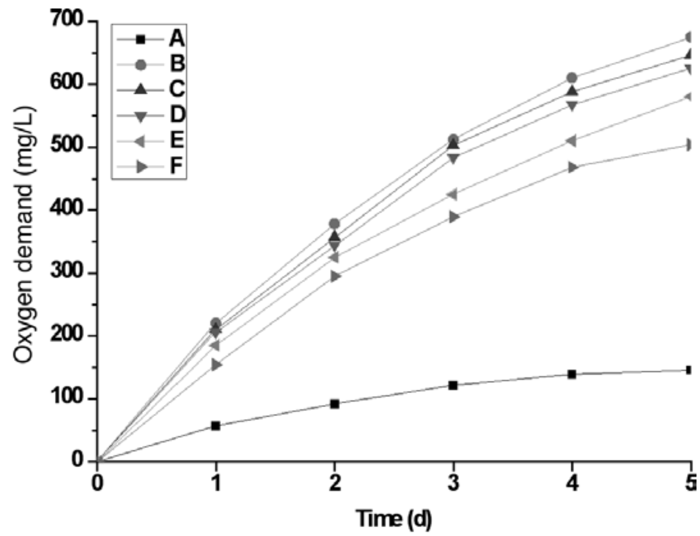


Figure 2. – The respiration curves of activated sludge in presence of rape oil-based fatliquors (phosphated: B; sulfonated: C; oxidized-sulphited: D; sulfated: E; copolymeric: F); A is the respiration curves of activated sludge.

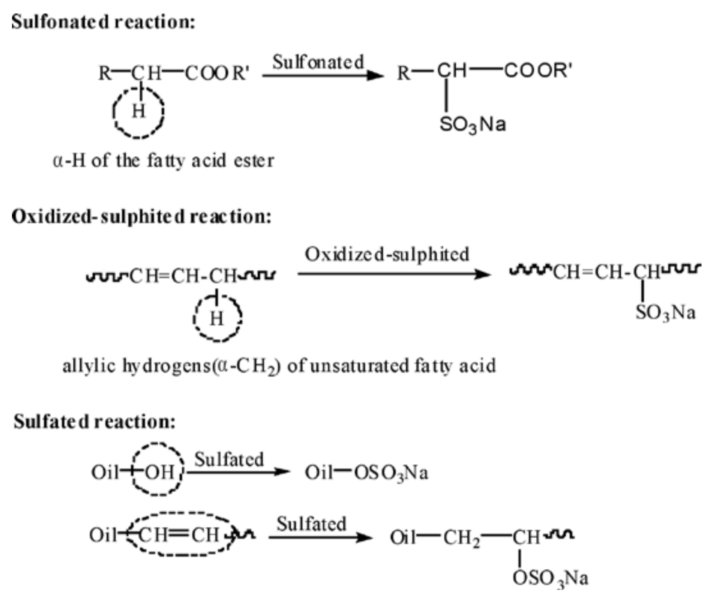


Figure 3. – Reaction positions of different modification methods.

intensively, whereas those of the sulfonated and phosphated fatliquors almost keep constant. This is due to the sulfated reaction (addition reaction) and free radical copolymerization consuming the double bonds, respectively, resulting in the iodine value in the two fatliquors decreasing. For oxidized-sulphited fatliquors, the decrease of iodine value should be attributed to the partial oxidative degradation decomposition of unsaturated fatty acids into small compounds with –CHO or –COOH.[24] However, in sulfonated and phosphated reactions, no double bonds are consumed, so sulfonated and phosphated modifications have little effect on iodine value.

Similarly, the change of hydroxyl group is also related to the modification methods. In the raw material, the hydroxyl value of rape oil is low, while after transesterification, the hydroxyl groups were generated, leading to the increase of the hydroxyl value. The hydroxyl value before and after different modification are shown in Table II. It can be seen that the hydroxyl values decrease for phosphated and sulfated reaction but stay unchanged for sulfonated and oxidized-sulphited reaction. This is because the former consumes the hydroxyl groups in modification process whilst the latter don't consume the hydroxyl group, therefore the hydroxyl value almost keep the constant.

The biodegradabilities of rape oil-based fatliquors

The biodegradabilities of the fatliquors under activated sludge were evaluated based on determinations of biological respiration curves, BOD_5/COD value, COD and TOC removal ratios. The respiration curves of sulfated, sulfonated, oxidized-sulphited, phosphated and copolymeric rape oil-based fatliquors as well as the endogenous respiration curve of the activated sludge are shown in Figure 2.

The respiration curves of activated sludge in present of rape oil-based fatliquors are all above the endogenous respiration curve, which means that all of them are biodegradable. And the respiration curve of activated sludge in presence of phosphated fatliquors is higher than others, while the copolymeric one is the lowest, indicating that the biodegradability of the phosphated rape oil-based fatliquors is the best, and the biodegradability of copolymeric fatliquors is not as good as the others.

As shown in Table III, the BOD_5/COD value is greater for phosphated fatliquors than for other fatliquors and are all higher than 0.45, showing that all fatliquors are biodegradable and show the biodegradability order of phosphated> sulfonated> oxidized-sulphited> sulfated> copolymeric.

Similarly, the COD removal ratio order of these fatliquors is phosphated> sulfonated> oxidized-sulphited> sulfated> copolymeric, and are all higher than 85%, showing good biodegradabilities and as the same order as the respiration curves. This conclusion can be further confirmed by the TOC removal ratio analysis. As can be seen from Table III, the TOC removal ratios of all the fatliquors are higher than 85%, indicating good biodegradable feature of them. Furthermore, the order of biodegradability is in agreement with the COD removal ratios.

The difference in the biodegradabilities of these fatliquors should be attributed to different active groups' content in the fatliquors after modification. For phosphated product the double bounds are hardly consumed in modification, higher double bounds in fatliquors are beneficial for their biodegradation. On the other hand, the blocked hydroxyl groups are set free during the biodegradation process due to the hydrolysis of phosphate ester in absence of microbial enzyme, which also increases its biodegradability; Another reason is that during the decay of biodegradation the nutrient element P, which is made available to subsequent generations of growing biota, is released, also accelerating the degradation of fatliquors.[25] That is why the phosphated fatliquors shows the best biodegradability.

For copolymeric fatliquors, it is another case. In one hand, the double bounds were consumed in the free radical polymerization which decreased its biodegradability. On the other hand, the copolymeric fatliquors, due to their large molecular size and steric effect are not easy to pass the phospholipid bilayers of the microorganism's cell membrane and combine with the active sites on the microbial enzyme,[26-27] which also decreased their biodegradation. So the biodegradability of copolymeric fatliquors is inferior in all resultant products. Just as mentioned above, the content of hydroxyl groups and the double bounds are higher for sulfonated and oxidized-sulphited fatliquors than for sulfated fatliquors, as a result, the biodegradabilities of the former are superior to the latter. This difference in the biodegradabilities is believed to be related to their reaction positions (described as figure 3).

The reaction positions of the sulfonated and oxidized-sulphited reactions are the α-H of the fatty acid ester and the allylic hydrogens (α-CH_2) of unsaturated fatty acids, respectively. Theoretically, the double bounds and hydroxyl groups are not consumed in these two cases, but actually partial double bonds are consumed for oxidized-sulphited reaction in the oxidation process, that is why the biodegradability of the sulfonated fatliquors is superior to the oxidized-sulphited fatliquors. However, in sulfated reaction, most of the double bonds and hydroxyl groups are consumed, so the biodegradability of sulfated fatliquors is inferior in the three products.

From the above analysis we find that different modification methods affect the space structure and active groups content of the resultant fatliquors, which affects their biodegradabilities. Although the biodegradation mechanisms of various fatliquors need to be further studied in detail, the prediction of the relationship between the structure and biodegradability of fatliquors will provide guidance for developing new environmental friendly fatliquors.

CONCLUSIONS

(1) These cumulative results indicate that the modification method is the most important issue associated with the biodegradabilities of rape oil-based fatliquors;

(2) The content of double bonds and hydroxyl groups in the fatliquors are mostly dependent on the modification methods, the one which consumes the double bonds or hydroxyl groups will decrease their biodegradabilities, whilst others which do not consume the double bonds or hydroxyl groups will impart the product better biodegradability;

(3) The biodegradability sequence of the rape oil-based fatliquors is: phosphated> sulfonated> oxidized-sulphited> sulfated> copolymeric.

Acknowledgments

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