



A practical approach based on FT-IR spectroscopy for identification of semi-synthetic and natural celluloses in microplastic investigation

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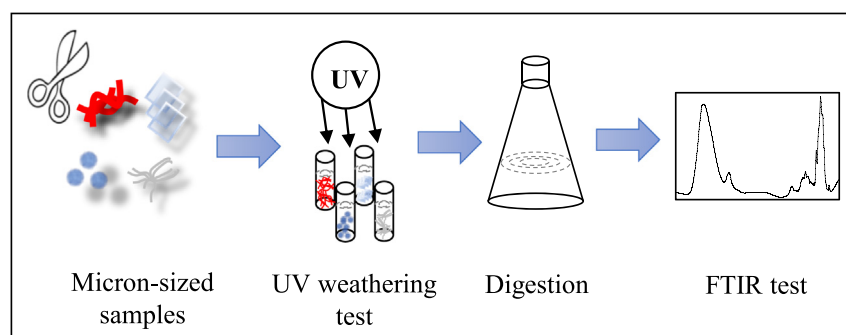
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HIGHLIGHTS

- Commercial products exhibited obvious changes after weathering and digestion.
- The band at 1105 cm^{-1} only existed in natural fibers even after treatments.
- The band at 1105 cm^{-1} provided a reference to differentiate semi-synthetic fibers.
- The enhanced library of polymer spectra was also proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

In previous studies of marine debris or microplastics (<5 mm), various types of semi-synthetic celluloses (e.g. rayon) are ubiquitous in some field investigations. However, it is hard to distinguish semi-synthetic and natural celluloses clearly even using the spectroscopic method. In this study, 8 semi-synthetic and 4 natural celluloses were employed as the test materials to simulate the environmentally relevant samples. Our results showed that these original commercial products exhibited obvious physical (e.g., color) and chemical (e.g., spectra) changes after UV weathering and agent (H_2O_2 and KOH) digestion treatments. The changes of 4 characteristic bands (1735 , $1425/1419$, 1105 , $1060\text{--}1053/1030\text{--}1027\text{ cm}^{-1}$) were evaluated. We found that the band at 1105 cm^{-1} which is assigned to the C—O antisymmetric in plane stretching band only existed in natural fibers even after the weathering and digestion treatments. The mixture of semi-synthetic and natural fibers from the real field samples was also easily distinguished using the characteristic band at 1105 cm^{-1} . Our results suggest that the characteristic band at 1105 cm^{-1} could be an ideal reference to distinguish natural and semi-synthetic fibers in field microplastic investigations. We also proposed a practical method to enhance the library of polymer spectra and improve the accuracy of semi-synthetic microplastic identification.

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1. Introduction

Microplastics (<5 mm) have been recognized as emerging marine pollutants due to their persistence (Kubota, 1994) and toxic potential (Endo et al., 2005; Engler, 2012). In recent years, microplastics have been widely studied and found in many environment systems including

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organisms, waters and sediments (Li et al., 2015; Lusher et al., 2015; Wesch et al., 2016; K appler et al., 2018). Microplastic investigation plays an important role in revealing the abundance, characteristics and fate of microplastic in real environments. Qualification and quantification analysis are the basis of microplastic study for field samples. So, it's essential to build and use reliable analytical methods for microplastic research.

In field investigations, a series of procedures including sampling, isolation and identification are required for analysis. Identification is a necessary process to ensure the polymer types of suspectable particles and reduce errors from previous observation. Three identification methods are commonly used in previous investigations. They are naked eye and/or microscope, combination of naked eye/microscope and instrument and identification of all counted particles by FTIR or Raman spectroscopy (Shim et al., 2017). In earlier microplastic studies, researchers usually identified particles through naked eye and/or microscope (Laglbauer et al., 2014; Talvitie et al., 2015; Sutton et al., 2016). In these investigations, particles can only be divided into plastics or non-plastics.

However, Song et al. (2015) point out that the error rate of this method is about 72%. Two different researchers using microscope and spectroscopy respectively obtain different results about microplastic pollution in beers (Liebezeit and Liebezeit, 2014; Wiesheu et al., 2016). After that, a more credible method is used in the identification of microplastics, i.e., a combination of naked eye/microscope and instrument in research (Hidalgo-Ruz et al., 2012; Imhof et al., 2012; Eriksen et al., 2013). In this method, limited numbers of suspectable particles are identified using Fourier Transform Infrared spectroscopy (FT-IR), Raman spectroscopy or scanning electron microscopy (SEM) with energy dispersive X-ray spectrometry (SEM-EDS). FT-IR and Raman are used to identify polymer types in a complementary manner (K appler et al., 2016). Alternatively, carrying out identification of all counted particles by FT-IR or Raman spectroscopy has also been recommended by some researchers (Vianello et al., 2013).

In previous investigations, microplastics (polypropylene, polyethylene, polyethylene terephthalate, polystyrene, etc.) are widely reported with identification (Fr ere et al., 2017; Matsuguma et al., 2017). However, some types of semi-synthetic cellulose (e.g., cellophane, rayon and cellulose acetate) show high prevalence in microplastic studies (Lusher et al., 2013; Remy et al., 2015; Frias et al., 2016; Li et al., 2016; Dris et al., 2017). These particles are cellulose-basic and their chemical features are similar to natural fibers such as cotton, sisal and jute, which makes it very hard to distinguish semi-synthetic and natural fibers (Peeken et al., 2018). In addition, researchers usually use commercial library provided by companies to obtain polymers types. However, commercial library may mix natural and semi-synthetic celluloses up. Thus, the abundance of semi-synthetic celluloses may be underestimated or overestimated in microplastic studies, which might affect the calculation of microplastic. Therefore, it is necessary to develop a creditable method to identify semi-synthetic particles.

Comnea-Stancu et al. (2017) developed a method to distinguish natural and semi-synthetic fibers using ATR (Attenuated Total Reflection)-FTIR. This is a useful way to help tell differences between natural and semi-synthetic fibers using characteristic bands concluded from commercial products. Nevertheless, the degradation of plastics is an important source of microplastics in environment, and the UV rays play a leading role in the degradation of the plastics. The physical and chemical characteristics of field samples are different from original products to some extent (Wang et al., 2016). And then samples are brought back to laboratory and digested roughly in field investigations. The gap between field samples and commercial products should be considered. As a consequence, it's very important to put forward a useful and practical method to distinguish between natural and semi-synthetic fibers in field samples.

In this study, micron-sized samples prepared in laboratory and real environmental samples were used to select the reference characteristic

band for distinguishing natural and semi-synthetic samples using FTIR with transmittance mode. We also tried to propose a suitable and practical method to enhance the library of polymer spectra and improve the accuracy of semi-synthetic microplastic identification.

2. Materials and methods

2.1. Micron-sized samples prepared in laboratory

Commercial products with known chemical composition were bought in textile market. Semi-synthetic cellulosic products included Cellophane, Rayon (Rayon1, Rayon 2), Modal, Tencel (Tencel 1, Tencel 2) and Cellulose Acetate (CA) (Table S1). Natural fiber products included Cotton (Cotton 1, Cotton 2, Cotton 3), Sisal and Jute. CA and Cotton 1 were bought from Sinopharm Chemical Reagent Co., Ltd., and other fibers were bought from Shaoxing Jujin (Yintai) Textile Co. Ltd. All these fibers were cut using scissors into beakers, and all the pellets were pulverized in a mortar and made particles as small as possible (Li et al., 2018). These samples were collected and passed through a 1mm mesh size sieve for further treatments.

2.2. Weathered and digested samples prepared in laboratory

Ultraviolet accelerated weathering treatment was performed on materials simulating environmental exposure for it could imitate the effect of natural weathering (Puterman, 1989). 0.5mg each material was put in a 30 mL glass bottle with 25mL ultra-pure water (Milli-Q), and then exposed to 302nm ultraviolet light for one week (Darie et al., 2015).

After weathering treatment, materials were dried and then transferred into glass flasks for digestion which is a necessary step to analyze field samples. Each weathered sample was divided into two parts and then digested with 30% (v/v) hydrogen peroxide (H₂O₂) (Jabeen et al., 2017; Qu et al., 2018) and 10% (w/w) potassium hydroxide (KOH) (Wiesheu et al., 2016; Hermesen et al., 2017), respectively. Both of these two methods are widely used in microplastic studies. 100 mL of digestion solution was poured into flasks and aluminum foil was used to cover the containers. Then the flasks were put into an oscillation incubator at 65 °C and 80 rpm for 72 h to accelerate H₂O₂ digestion, or at 60 °C and 80 rpm for 72 h to accelerate KOH digestion. All containers and tools were rinsed with Milli-Q three times before use to avoid contamination. After digestion, the remaining samples in the liquid were obtained through 5 μm filter membrane (Millipore SMWP04700) for further analysis.

2.3. Extraction and isolation of particles from the field

Water samples were collected from rivers in Shaoxing, Zhejiang province (S₁-S₅) (Fig. S1). The sampling areas and individual sampling spots are near to the textile plants and textile distribution centers, which suffer from different types of pollutants. The extraction and isolation method of samples was followed by Su et al. (2018). In brief, the surface water samples were poured through 20 μm nylon net filter (Millipore Nylon NY2004700). And then the particles on the filter were washed into a glass flask using 100 mL of 30% (v/v) H₂O₂ for digestion. The glass flasks were covered by aluminum foil and placed in an oscillation incubator at 65 °C and 80 rpm for 72 h. After digestion, the liquid in flask was filtered through a 5 μm filter membrane (Millipore SMWP04700) and the filter membrane was stored in a dry petri dish for observation and identification later.

2.4. Observation, identification of polymer composition and library enrichment

All samples were observed under a Carl Zeiss Discovery V8 Stereo microscope (MicroImaging GmbH, G ttingen, Germany), and images were taken with an AxioCam digital camera (Yang et al., 2015). The

chemical composition of original samples was confirmed with spectra of standard materials using μ -FTIR (Nicolet iN 10, Thermo Fisher with transmittance mode, microcompression cell II with diamond windows, spectral resolution: 4 cm^{-1} , 32 scans, Table S2, Fig. 1). The algorithm used in result matching was “Similarity Matching” because it was recommended and could eliminate the effects of baseline variation in unknown spectra (operation manual provided by company). The spectrum of each original sample was normalized and renamed, then added into searching library to enrich the commercial library. The identification results of the commercial products with improved library were more accurate than before (Table S3). Both the spectra and the matching accuracy of treated samples were acquired on this instrument with the improved library using the spectral range of $4000\text{--}600\text{ cm}^{-1}$ (Li et al., 2016). The composition of field samples was confirmed using the same FTIR parameters as those used for original samples above. The lowest acceptable Hit Quality was set as 70%.

2.5. Spectral analysis and the development of characteristic band method

The chemical information of samples after treatments was collected. Each treatment was performed in triplicate. The correlation values referred to the spectral similarity between treated and original samples were obtained in OMNIC software, and the sensitivity of this process was consistent with the matching process in identification part. Then

the average of triplicate correlation values was obtained and subtracted from 1, and the result was called Variability Value to represent the variability of samples after treatments. Atmospheric correction was conducted in spectra to deduct the effect of carbon dioxide. The “Find peaks” function in OMNIC software was used to obtain the x-coordinates of characteristic band peaks. The sensitivity (100) and the threshold (0.02) were set to make all peaks be signed in annotate results.

The identification method of semi-synthetic and natural samples was inspired by Comnea-Stancu et al. (2017) and has been ameliorated. For transmittance mode, the band at 1732 cm^{-1} can only be seen in some natural fiber samples (Singh et al., 2015) and it is related to pectin content. Natural fibers have a strong band in 1431 cm^{-1} (Oh et al., 2005) because of CH_2 symmetric bending and it turns to be weak and shifted to 1420 cm^{-1} for semi-synthetic fibers (Carrillo et al., 2004). Additionally, absorption bands at 1100 cm^{-1} (Abidi et al., 2014) assigned to the antisymmetric C—O—C in plane stretching band and $1053\text{--}1058/1030\text{--}1034\text{ cm}^{-1}$ (Uçar et al., 1996) for C—O—C and C—O stretching modes, these two bands show high intensity for natural fibers but only the later band shifts to 1035 cm^{-1} (Carrillo et al., 2004) in semi-synthetic samples. However, for commercial products, bands may shift and be different from literature data. As a result, adjusted characteristic bands were employed to develop characteristic band method.

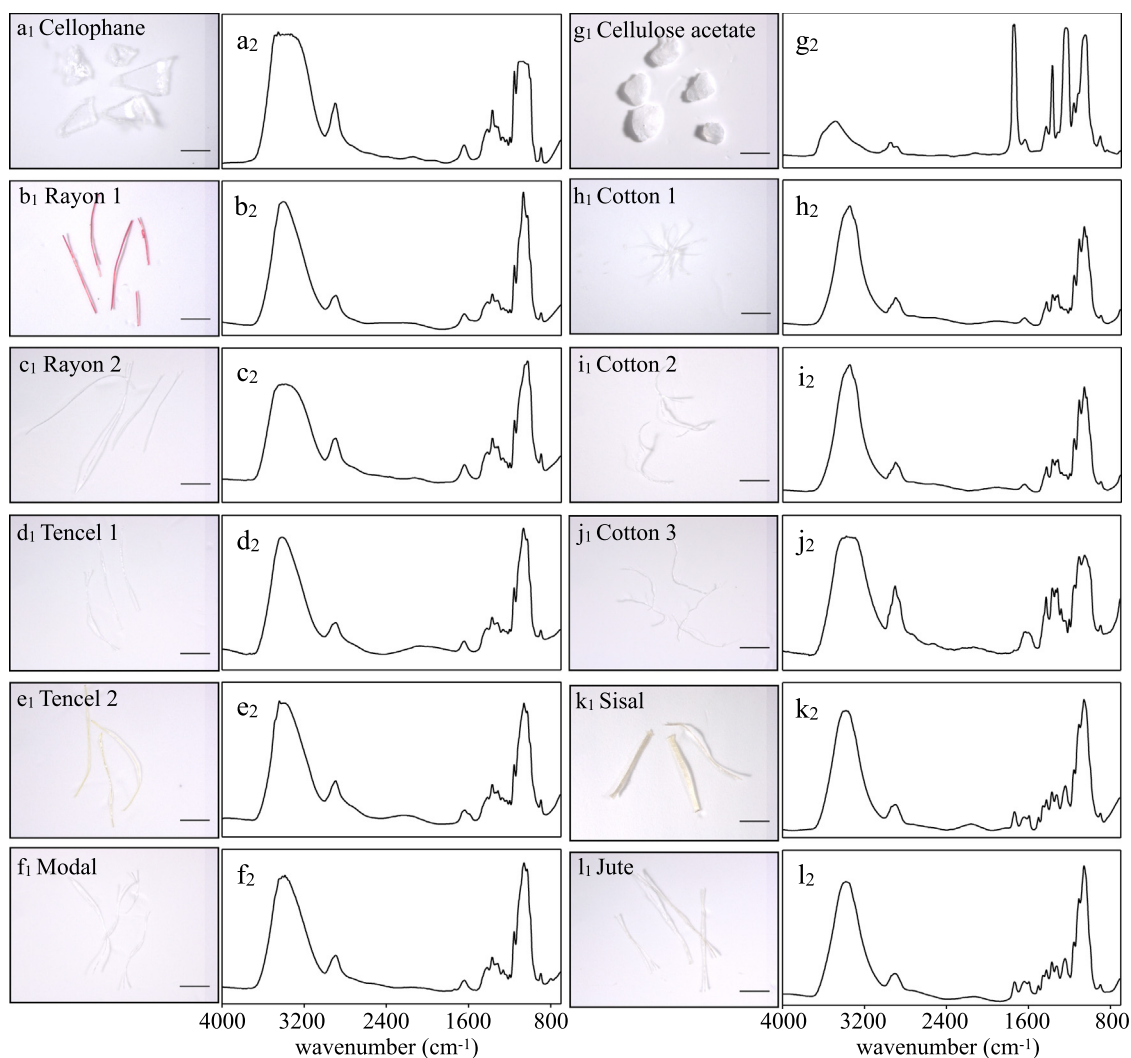


Fig. 1. The morphology and spectra of twelve types of particles prepared in laboratory. (a). Cellophane, (b). Rayon 1, (c). Rayon 2, (d). Tencel 1, (e). Tencel 2, (f). Modal, (g). Cellulose acetate, (h). Cotton 1, (i). Cotton 2, (j). Cotton 3, (k). Sisal, (l). Jute. Scale bar = $150\text{ }\mu\text{m}$.

A cursory appraisal method of band position shifts after treatments was used in spectral analysis: band disappeared (0), band shifted 6–10 wavenumber (1), band shifted 1–5 wavenumber (2), and band shifted 0 wavenumber or also inexistent (3) (Fig. S2). The score of each species was calculated according to Eq. (1),

$$\text{Score}_{\text{Total}} = \text{Score}_{\text{species-W}} + \text{Score}_{\text{species-H}} + \text{Score}_{\text{species-K}} \quad (1)$$

W means weathering treatment; H means the H_2O_2 digestion; K means the KOH digestion; Species stands for 12 cellulosic samples (3

replications for each). The higher the score was, the more stable the characteristic band was.

3. Results

3.1. Physical and chemical changes of the particles prepared in laboratory

Four groups of samples (Cellophane, CA, Sisal and Jute) had obvious changes in morphology and spectra (Fig. 2). For weathering treatment, samples still kept original morphology features but had changes in spectra (Fig. 2a₁' , b₁' , c₁' , d₁'). For digestion of weathered samples, H_2O_2 had

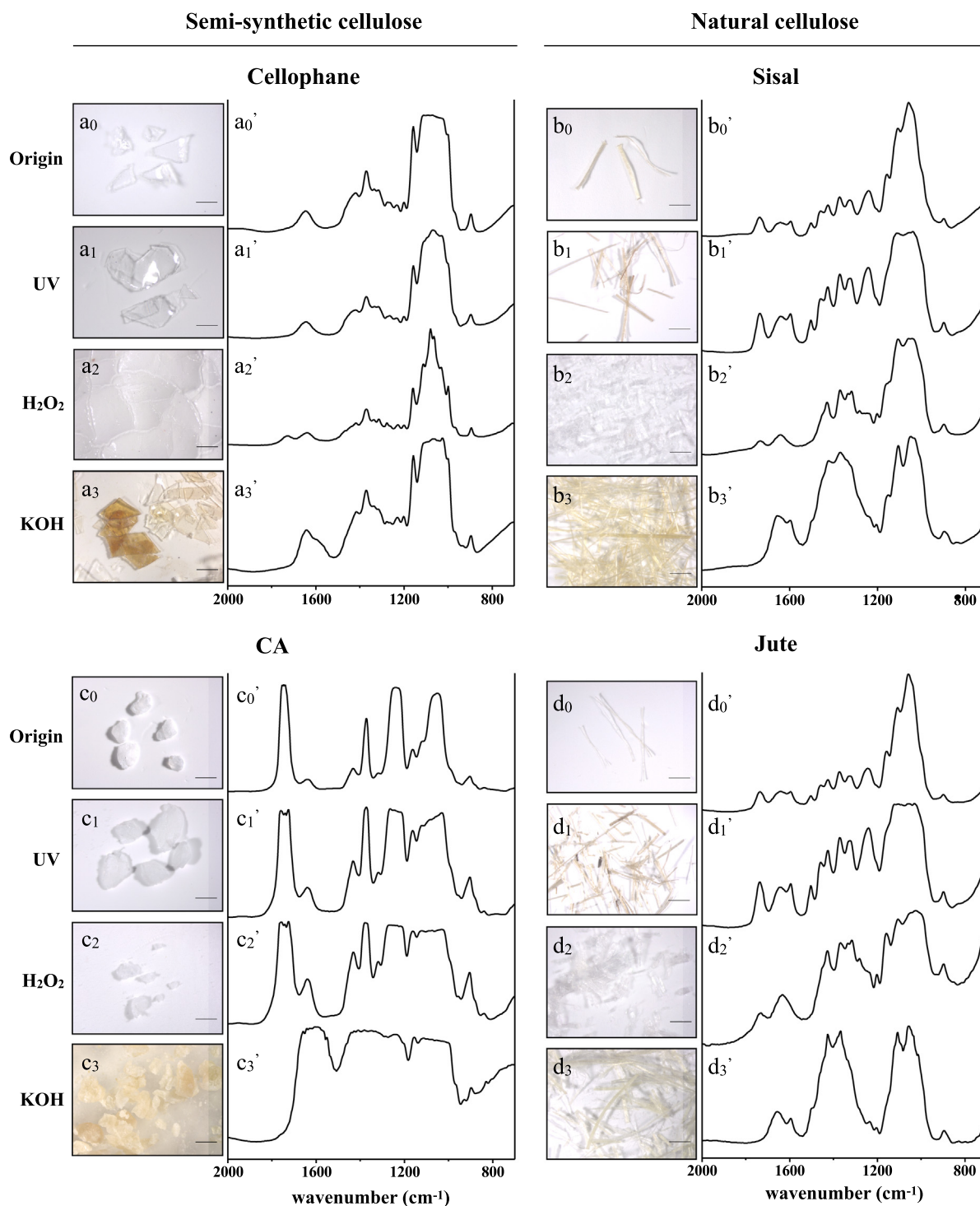


Fig. 2. The morphology and spectra change of samples. (a). Cellophane; (b). Sisal; (c). CA; (d). Jute. Scale bar = 150 μm.

discoloration effect on sisal and jute (Fig. 2b₂, d₂) and KOH made Cellophane and CA yellow (Fig. 2a₃, c₃). In addition, Cellophane was no longer solid but some paste on filter (Fig. 2a₂) after H₂O₂ digestion, and this phenomenon only showed in cellophane groups. Both H₂O₂ and KOH digestion changed the spectra of samples toughly.

The average of 3 Variability Values was used to indicate spectral changes of the samples treated with environmental factors (Fig. 3). All the samples were changed after weathering and digestion treatments and showed differences in their IR spectra from the original material. Rayon 2 showed the lowest Variability Value amongst samples in weathering group (about 3.0%). The highest Variability Value in weathering group was Cotton 3 (about 28.2%). For H₂O₂ digestion, the lowest Variability Value presented in Rayon 2 (8.0%) and the highest in Tencel 1 (42.0%). For KOH digestion, the lowest Variability Value presented in Cotton 2 (10.8%) and the highest in CA (92.1%).

3.2. The evaluation of adjusted characteristic bands based on environmental relevant samples

A further identification was carried out to tell the differences between natural and semi-synthetic celluloses. According to the characteristic bands of commercial products, 4 adjusted bands were employed in experiment (Fig. 4). However, in semi-synthetic cellulose samples, CA had band at 1735 and 1052 cm⁻¹ but didn't have band at 1419 cm⁻¹. In natural fibers, Cotton 1, Cotton 2 and Cotton 3 didn't have band at 1735 cm⁻¹.

The adjusted characteristic band position was used to evaluate samples with environmental factors treatments (Fig. 5). In the second adjustment, the band at 1105 cm⁻¹ for antisymmetric C—O—C in plane

stretching had the highest score (272) of four types of characteristic bands based on the calculation of Eq. (1). The second one was the band at 1735 cm⁻¹ (267), and this band presented in CA, Sisal and Jute but disappeared after KOH digestion. However, other natural cellulose products didn't have this band. The third one was band at 1419 or 1425 cm⁻¹. Although this band didn't disappear after all treatments, its position shifted a lot in samples' spectra (237). The last one was band of C—O—C and C—O stretching (1060–1053/1035–1027 cm⁻¹, 197), and its position shifted a lot and even disappeared in some treatment group (Cellophane and Jute). The band of antisymmetric C—O—C in plane stretching at 1105 cm⁻¹ had minimal change and still showed significant differences between natural and semi-synthetic samples after weathering and digestion treatments. This adjusted characteristic band position is suitable for samples digested with H₂O₂ and KOH.

3.3. Examination of field samples

In this study, 105 cellulosic field samples were examined. The characteristic band at 1105 cm⁻¹ could still tell the differences between natural and semi-synthetic fibers in field samples clearly (Fig. 6). Sample a (S₁) had a sharp band at 1105 cm⁻¹, and Sample b (S₅) had a peak at 1103 cm⁻¹ with only 2 cm⁻¹ shifting. However, Samples c (S₂) and d (S₃) had no band or just a shoulder-like band at 1105 cm⁻¹.

In addition, we added the spectra of 12 products' spectra to the commercial library (i.e., the improved library). The compositions of samples were obtained using the commercial library. Besides typical plastics like PET, PP and PE, five types of semi-synthetic and natural fibers were matched, and they were Cellophane, Paper, Cotton, Cellulose and Linen. Although there were some types of celluloses, the software

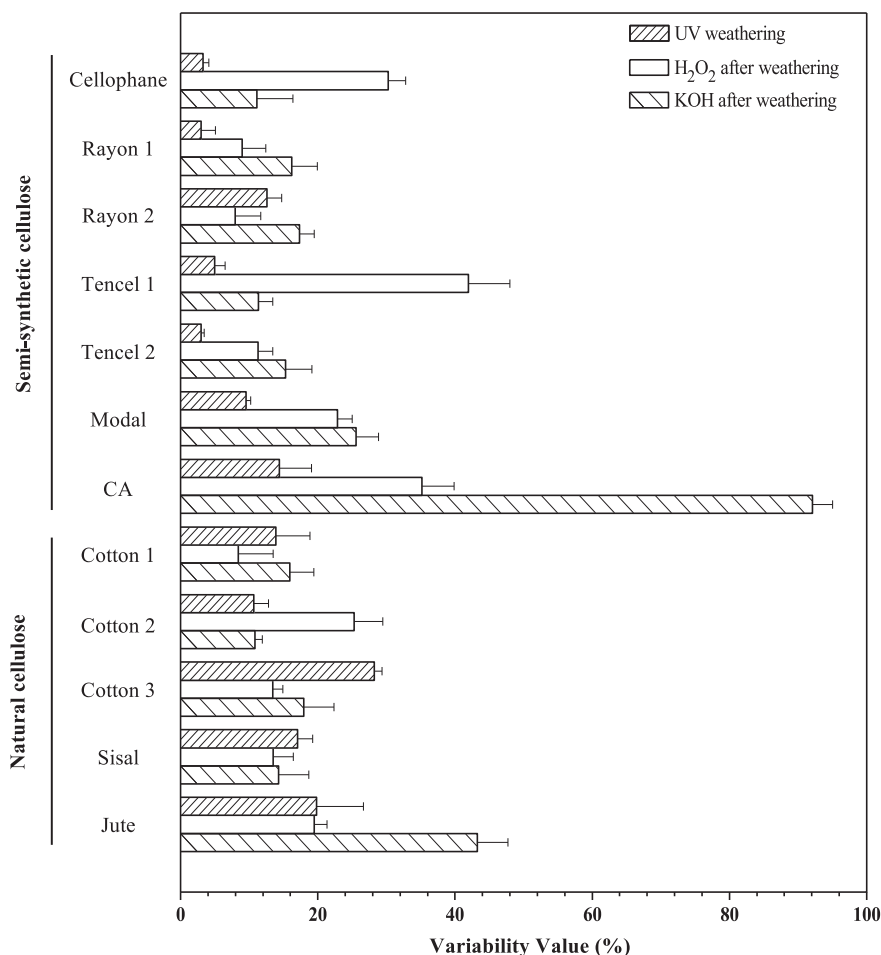


Fig. 3. The Variability Values of 12 types of cellulosic materials after environmental relevant sample treatment.

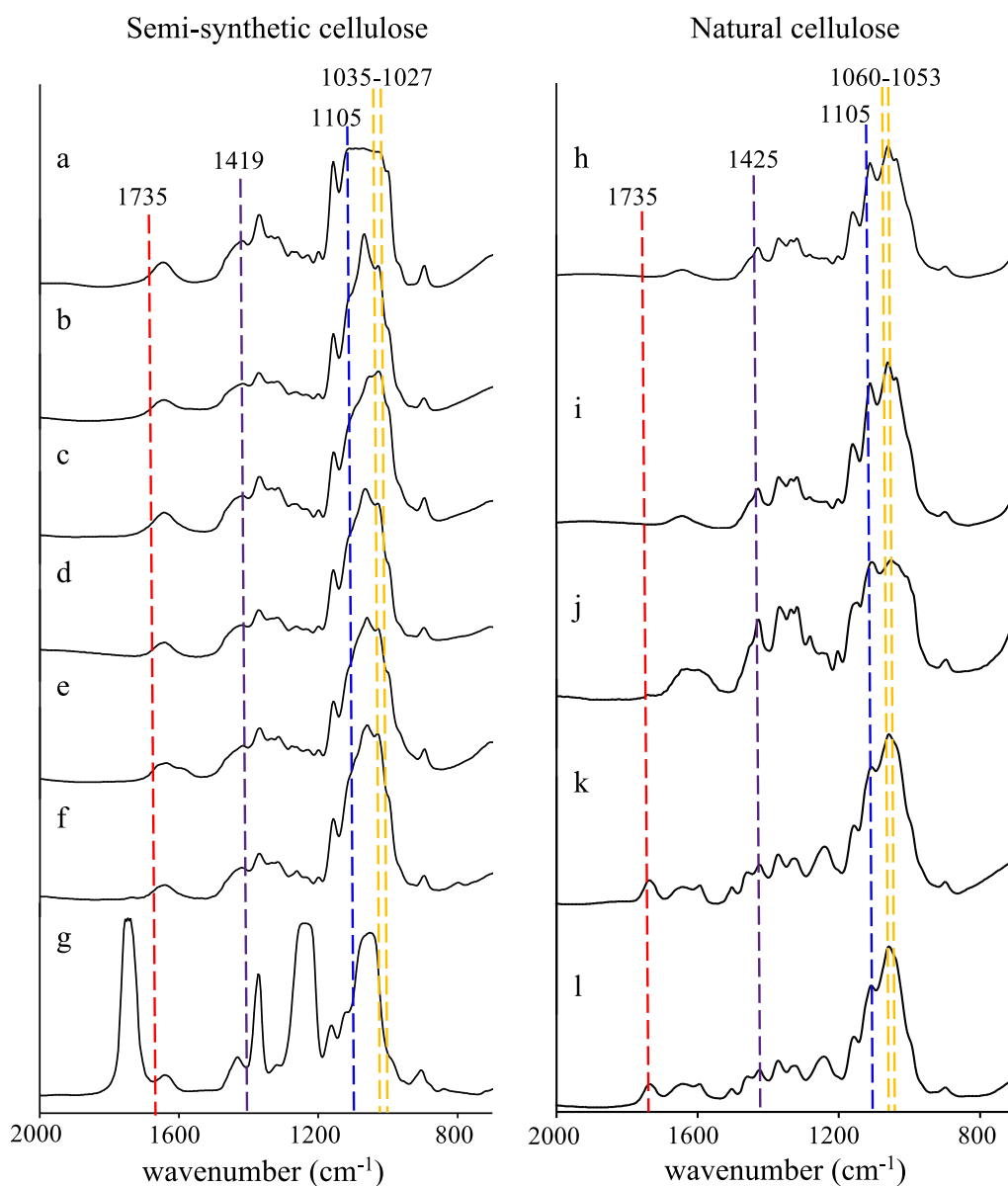


Fig. 4. Adjusted characteristic bands of FT-IR spectra related to 7 semi-synthetic cellulose samples (a–g) and 5 natural fiber samples (h–l): (a). Cellophane, (b). Rayon 1, (c). Rayon 2, (d). Tencel 1, (e). Tencel 2, (f). Modal, (g). CA, (h). Cotton 1, (i). Cotton 2, (j). Cotton 3, (k). Sisal, (l). Jute.

confounded the natural fibers with and semi-synthetic ones. Another three types were also matched (Rayon, Sisal and Jute) and the types of celluloses were corrected using the improved library. In all, the abundance of natural fibers increased from 3.2% to 11.8%.

4. Discussion

4.1. The characteristic band for distinguishing natural and semi-synthetic fibers

Microplastics in field samples have been toughly weathered and digested when we try to identify them. In this study, environmental relevant samples instead of origin commercial products were used to find the valid method for distinguishing natural and semi-synthetic fibers. In our study, after UV accelerated weathering treatment and digestion, the laboratory-made samples truly changed in morphologic and spectroscopic features, and theoretically became more similar to actual field samples. Hence, we recommend to use environmental relevant samples

for methodological development in research. This idea is also in line with Karami in his aquatic toxicological study (Karami, 2017).

Four strong characteristic bands indicating four different chemical functional groups under transmittance mode were selected from literature data, and then they were inspected after the samples were treated in laboratory in this study. After evaluation and marking of each band, the characteristic band of antisymmetric C–O–C in plane stretching near 1105 cm^{-1} showed higher stability than other characteristic bands. Except that, the band at 1105 cm^{-1} only existed stably in all spectra of natural samples and was never found in semi-synthetic samples. This phenomenon was also an important reason for us to recommend the band at 1105 cm^{-1} for researchers to distinguish natural and semi-synthetic fibers, because it is easy and practical to check one band position in identification. Meanwhile, it's not time consuming to inspect if the spectrum of a sample has a peak or not with the help of software. All functions used in this method are basic configuration in spectral software. Usually this process only costs several seconds.

When characteristic method was applied to field samples, we could determine which ones are celluloses based on the spectra and

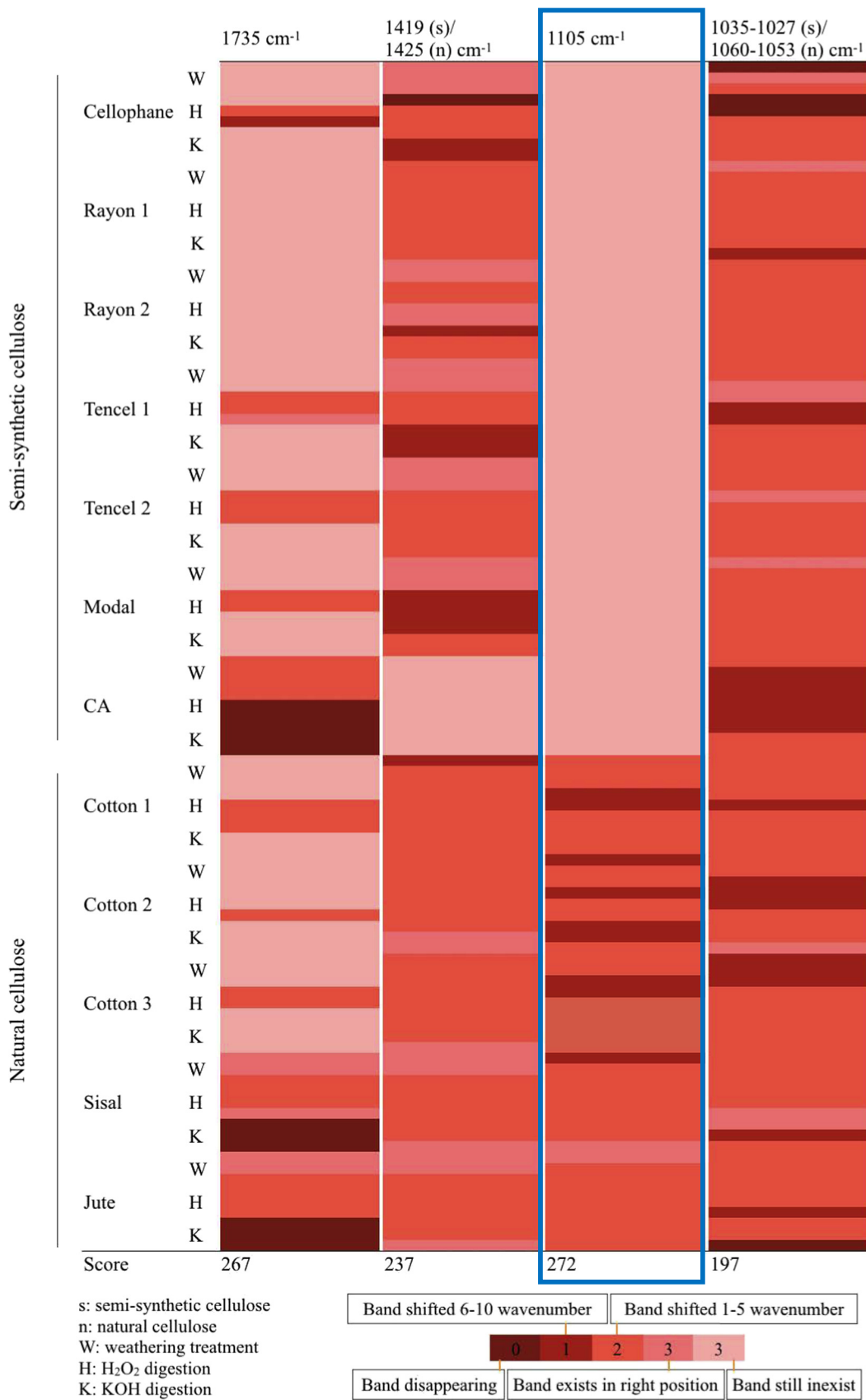


Fig. 5. Results of treated samples by using characteristic band method. Red and gray blocks score 3 points and stand for bands having no changes. Light red blocks score 2 points and stand for bands shifting in 1–5 wavenumber. Pink blocks score 1 point and stand for bands shifting in 6–10 wavenumber. Black blocks score 0 point and stand for bands disappearing. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

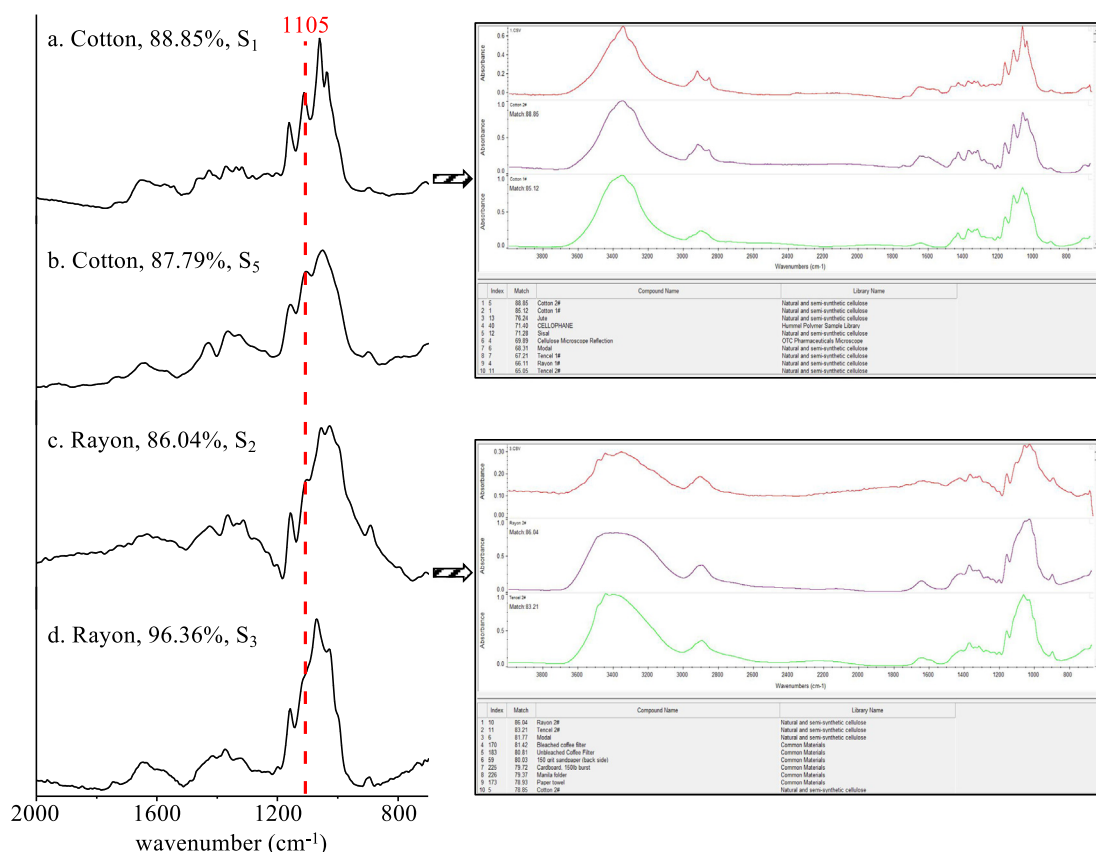


Fig. 6. Four field samples' spectra after laboratory treatment and matching results with improved library. The band at 1105 cm⁻¹ can distinguish natural and semi-synthetic fibers clearly.

preliminary matching results of unknown particles. For these spectra of cellulosic fibers (Hit Quality ≥ 70%), the characteristic band method should be used to differentiate semi-synthetic and natural celluloses because spectral software cannot tell their difference clearly. In this study, the band of antisymmetric C—O—C in plane stretching near 1105 cm⁻¹ still existed and could be used to distinguish semi-synthetic and natural fibers in field investigation. However, this characteristic band method has a limitation that it cannot tell the ratio of natural and semi-synthetic celluloses if samples contain both natural and semi-synthetic and even synthetic fibers. So, the quantification technology should be used for further identification. However, it should be semi-synthetic one, and the error decreases in identification part if 1105 cm⁻¹ doesn't exist in a cellulosic fiber.

Therefore, to differentiate between semi-synthetic and natural fibers in field investigations at present, it is more suitable to use a strong and stable characteristic band (1105 cm⁻¹) concluded from environmental relevant samples. Of course, it is a practical way to check one band position with the help of software during the identification process.

4.2. The limitations of commercial library for FTIR

For microplastic identification, researchers usually rely on commercial library which is predefined in software and few of them have their own library (Obbard et al., 2014; Alomar and Deudero, 2017). Usually, the complex samples in environment have various composition, bio-fouling, are weathered greatly or various types of cellulosic particles. There will be possibility that they can't be identified successfully with the matching algorithm and spectral library of instrument (Araujo et al., 2018). Some researchers appeal for modified or weathered polymer reference database (Huppertsberg and Knepper, 2018) and improved algorithm of matching progress in software. However, it's still a tough work to obtain standard weathered polymer samples or

accordant libraries. There is no standard library for researchers. For now, adding local products into commercial library is a better way to obtain more abundant and diverse results in microplastic studies.

Up to date, few investigations documented detailed library used in studies. In 280 field investigations of microplastic from 2004 to 2018, 159 of them are conducted with instrument for identification of microplastic; cellulosic samples occur in 71 of them; detailed library names are only documented in 14 of them (Fig. 7). Unmentioned library is a potential problem in microplastic studies because different libraries lead to different results and make them incomparable. An accordant and suitable library could be necessary to compare results in researches. Our results suggest that enriching library is a convenient and practical solution for researchers when their library is scarce compared with others.

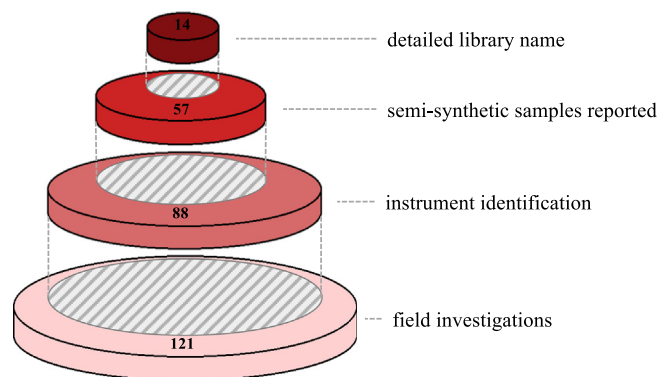


Fig. 7. In 280 field investigations from 2004 to 2018, 159 investigations used instrument for identification and 71 of them reported natural and/or semi-synthetic celluloses, 14 of them documented the detailed library name in studies.

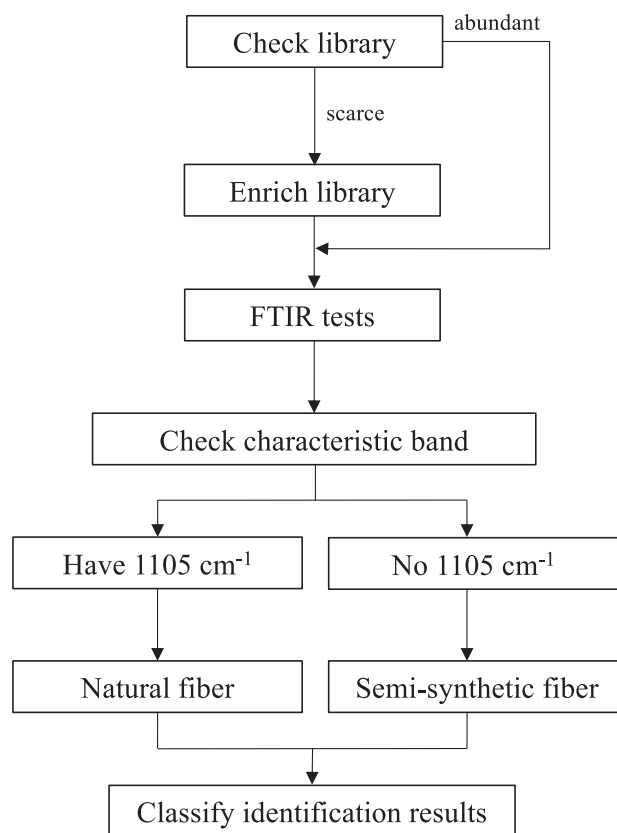


Fig. 8. The flow chart of the credible method for distinguishing natural and semi-synthetic fibers in microplastic identification.

It's helpful in distinguishing natural and semi-synthetic fibers in field studies.

4.3. Development of a suitable and practical method to differ natural and semi-synthetic fibers

On the basis of analysis on environmental relevant samples, a suitable and practical method was designed for researchers to decrease error rate in identification (Fig. 8).

- 1) Improving the library if it is lack of cellulosic materials. First, you should buy standard materials from local synthetic fiber research institute or products which have known composition and add their information into database for improved library.
- 2) Using characteristic band method to identify each valid result (Hit Quality $\geq 70\%$) of cellulosic sample. Check the band at 1105 cm^{-1} , if the sample has a peak at this position, it should be natural fiber; if the sample doesn't have a peak or only have a shoulder peak at this position, it should be semi-synthetic fiber.
- 3) Processing data and classifying fiber types. When the samples with a peak at 1105 cm^{-1} are identified as semi-synthetic fibers, they should be rectified as natural ones. On the contrary, the samples without 1105 cm^{-1} should be semi-synthetic fibers despite natural ones from matching results.

After all these 3 steps, researchers will obtain completed data and distinguish semi-synthetic and natural fibers clearly.

5. Conclusions

In microplastic investigation, it is a challenge to distinguish semi-synthetic and natural celluloses clearly. In the present study, we

simulated the environmentally relevant particle samples and analyzed the changes of characteristic bands using FTIR. Our results suggest that the characteristic band at 1105 cm^{-1} could be an ideal reference to distinguish natural and semi-synthetic fibers in field microplastic investigations. Combining characteristic band method with enhanced library of polymer spectra is a suitable and practical method to improve the accuracy of semi-synthetic microplastic identification. Our work makes identification more practical, suitable and credible for microplastic studies. In future, more characteristic bands should be dug out to help differentiate microplastics which have similar or complex chemical structure. More efforts should be put on standard, accordant and suitable libraries for microplastic studies.

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2019.03.124>.

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