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Reflux extraction and analysis of polyethylene wax in soil *

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Abstract: An efficient reflux extraction of polyethylene wax (PEW) in soil is presented, followed by molecular structure characterization methods to explore its degradation mechanism. To more realistically simulate the actual degradation of PE film powders in soil, low density PE (M=5 000) powders, being used as simulated PEW residue sample, were uniformly mixed with soil and then recovered by reflux extraction with decahydronaphthalen (decalin) at 90 °C for 60 min. The average recovery of PEW from fortified soils was 96.5% with the developed reflux extraction procedure. The recovered PEW residue samples were characterized by infrared spectroscopy (IR), element analysis (EA), X-ray fluorescence (XFR), and high-temperature gel permeation chromatography (GPC). The results from spectra analysis show that there were no significant changes in molecular structures and molecular mass distribution of PEW samples after the reflux extraction, which demonstrate the reliability of this method. These results also indicate that the reflux extraction procedure and analytical methods of characterization could serve as a novel measurement technique to evaluate the degradation of low-density PE powders in soil over time.

Keywords: polyethylene wax; reflux extraction; decalin; soil; biodegradation

Introduction

The growing use of plastics in agriculture for disposable items has been creating serious disposal problems. Non-degradable polymers tend to accumulate as plastic wastes and end-up in landfills, challenging waste management in limited landfill sites. To reduce the accumulation of plastic wastes, manufactures have formulated various degradable plastics since 1970s. Polyethylene (PE), one of the most widely used plastics, accounts for more than 50% of the plastic wastes. One of the focuses of early research in evaluating the biodegradation of PE waste was to investigate undesired changes in appearance and physical properties of plastics [1-8], as well as the
possible impacts on soil and plants. The biodegradability of agricultural plastic films has been studied by collecting samples at different time after the exposure in agricultural fields [9] or cultivated with microorganisms in the lab [10-13].

Previous studies have revealed that PE plastic films can be degraded by several mechanisms including photodegradation, thermooxidative degradation and biodegradation. PE films residue fragments can break down to powders in a short period by the synergistic action of light, heat, water, air and microbes in the environment [14-18]. PE film fragments can rapidly decompose to lower molecular mass powders on the surface of soil [19-20]. Ideally, a fully biodegradable PE plastic should be completely converted by microorganisms to mineral, biomass, carbon dioxide and water. However it is still not clear whether the PE powder residues in soil would go through ultimate degradation (mineralization), or how long it would take for the complete biodegradation. There have been no standard measurement techniques to evaluate the complete biodegradation of low density PE. Few studies have been reported to determine the degradation of PEW residue powders in soil. To more realistically measure and understand the degradation of PE powders in soil requires an efficient method for recovering the PE residues from soil and solid characterization of the molecular and chemical structure changes of PE residues in soil over time.

Herein we present a reflux approach by using decalin as a solvent to extract PE powder residues from soil and analytical methods for the molecular structure characterization of PE samples by Fourier transformation infrared spectroscopy (FT-IR), high-temperature gel permeation chromatography (HT-GPC), element analysis (EA) and X-ray fluorescence (XRF). The use of combined spectra analysis makes it realizable to provide the accurate and direct measurements of chemical structure changes and molecular mass breakdown of PEW powders in the soil, which could serve as a fundamental but novel analytical method to elucidate the degradation of PEW particle residues in soil.

2 Experimental

2.1 Reagents and Apparatus

Three different soils (clay, sand and loam) were collected from Mianyang, Sichuan, P. R. China. The PEW powders were purchased from commercial sources in Mianyang. Other chemical regents were obtained from Chengdu Kelong Chemical Reagent Factory, Chengdu, P. R. China. An infrared absorption spectrophotometer (IR) BSA124S (Thermo Nicolet Corporation, America) was used to determine the specific functional groups of the PE samples. HT-GPC analysis of samples was performed by gel permeation chromatograph 150-C (Waters, America). TG analysis of samples was conducted with a SDT 600 (TA, America) thermal analyzer at an air flow rate of 100 mL min⁻¹ in which samples were heated at a rate of 10 °C min⁻¹ from room temperature to 600 °C. X-ray fluorescence spectrometer (XRF) axios (PANalytical, Holland) and CHNS/O Elemental Analyzer (EA) EA3000 (EuroVector, Italy) were employed to detect the elements of the PEW samples.

2.2 Extraction methods

Collected soil samples were pretreated by removing stones and other impurities such as animal and plant residues. After being dried for several hours, the soil was smashed into powders, followed by the addition of a proportional amount of PEW powders \( m_1 \) and mix with each other evenly. To a three-neck flask, 30 g of such mixture of PEW and soil powders and 60 mL decalin were added. The solution was heated under reflux, with vigorous stirring, for 30 min to 90 min. The resulting mixture was filtered under vacuum to
separate the soil and the PEW samples dissolved in decalin. Additional decalin (30 mL) and absolute ethyl alcohol (20 mL) were used to wash the soil a few times to elute the remaining PEW samples. Then, the obtained PEW filtrate solution was poured into a clean separatory funnel. The bottom layer containing the PEW precipitates was poured into an empty, clean, dry petri dish \( (m_3) \) and dried at 60°C for 3 days, to achieve constant mass \( (m_3) \).

The recovery rate of PEW \( (w) \) was calculated by the following formula (1).

\[
w\% = \frac{(m_3-m_2)}{m_1} \times 100 \quad (1)
\]

3 Results and discussion

3.1 Selection of temperature for reflux extraction

To prevent the decomposition and oxidation of PEW sample during reflux extraction, the thermal stability of PEW was investigated to determine the optimal temperature of reflux extraction. TG analysis of PEW \( (M=5000) \) was performed on an SDT600 thermal analyzer, and the results are shown in Fig. 1. It is shown that a phase transition to liquid phase of PEW \( (M=5000) \) occurs near 110°C. Therefore, the reflux temperature can be around 110°C. To prevent the breakdown and oxidation of PEW, a reflux temperature of 90°C was used in the experiment.

3.2 Effect of the number of reflux extractions and the extraction time on recovery

Typically with the same total amount of solvent, multiple extractions with smaller amounts of solvent are more efficient than a single extraction. To maximize the recovery rate of PEW samples, we performed multiple extractions and measured the recovery rate of PEW sample by varying the number of extraction. Fig. 2 indicates the effect of the number of extractions on the recovery rate of PEW samples. The results show that the recovery increased significantly with an increase in the number of extractions until the number reached 3. There was no significant increase in the recovery when the number of extractions was more than 3. As a consequence, three reflux extractions are optimal and enough to achieve the maximum recovery.

We also conducted experiments to check the influence of the extraction time on the recovery. Fig. 3 shows the recovery increasing with an increase in extraction time from 30 min to 60 min. After 60 min, a plateau for recovery was obtained. The results indicate that 60 min of reflux was adequate to completely extract PEW.

3.3 Effect of soil type on the recovery of PEW sample

Table 1 lists the recovery of PEW \( (M=5000) \) powders in the 3 types of soil (clay, sand and loam), and the blank control, in which no soil was added. As can be seen from Table 1, there was no significant difference observed in recovery of PEW treated by different soil. The similar recovery (>95%) obtained with different soils indicated that our extraction method was efficient, rugged and robust. The reproducibility is satisfactory (RSD<1%). Compared with the method we have reported [21], the reflux extraction method is not only simple, but also with a high recovery rate.
3.4 Elemental analysis of the PEW before and after the reflux extraction

Table 2 lists the elemental analysis results of PEW (M=5 000) recovered from 3 types of soil and the blank control. The results show that the ratio of C/H and the total amount of C+H elements of the PEW samples extracted from the soil were very close to those of the blank control.

In addition, XFR was used to determine the impurity of the PEW samples recovered from soil. The results of the impurity of PEW samples recovered from the 3 types of soil are listed in Table 3. Both the PEW sample extracted and the blank control had a purity of 99%, which indicates that there was no significant change of impurities in PEW before and after the extraction. The main impurity of PEW is SiO₂. In the PEW sample recovered from soil, the impurity of CaO, P₂O₅ and Al₂O₃ decreased remarkably, and with absence of ZnO as compared to the blank control. The extractions brought in other impurities from soil: Fe₂O₃, K₂O and MgO in Loam. These impurities were, however, in trace amount, which would not likely affect the molecular mass measurement of PEW samples. Results of both element analysis and impurity analysis indicate the reflux extraction with decalin was effective and very specific for recovering the PEW residues in soil.
Table 2 Mass fraction (x) by Elemental analysis of the PEW before and after the reflux extraction

<table>
<thead>
<tr>
<th>Elements</th>
<th>x_C/%</th>
<th>x_H/%</th>
<th>x_C+H/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEW Blank</td>
<td>86.00</td>
<td>5.70</td>
<td>91.70</td>
</tr>
<tr>
<td>Sand</td>
<td>85.40</td>
<td>4.52</td>
<td>89.92</td>
</tr>
<tr>
<td>Loam</td>
<td>85.50</td>
<td>6.50</td>
<td>92.00</td>
</tr>
<tr>
<td>Clay</td>
<td>85.80</td>
<td>4.42</td>
<td>90.22</td>
</tr>
</tbody>
</table>

3.5 Structure characterization of the PEW by FT-IR before and after the reflux extraction

To investigate whether the structure of PEW changed before and after the extraction process, the structures of the recovered PEW samples were characterized by FT-IR spectroscopy. Fig. 4 is the FT-IR spectra of the PEW samples before (shown as a-blank) and after the extraction from soil. It is clearly shown that there was no new absorption peak emerged. Also in comparison to the blank control, no original absorption peak disappeared during the extraction, indicating that the molecular structure of PEW did not change before and after the extraction process.

3.6 Molecular mass distribution analysis of the PEW by HT-GPC before and after the reflux extraction

The molecular mass distributions of PEW samples before (shown as the blank control) and after the extraction process were measured by HT-GPC. The analysis results are presented in Fig. 5 and Table 4. Fig. 5 shows no significant change in the molecular mass distributions of PEW samples in the blank control and after extracting from three types of soil. The majority PEW molecular mass distribution was in the range of 3 000 to 6 000. The average molecular mass and average distribution fraction (D) of PEW after the extraction were 5097 and 1.69, which matched very well with the molecular mass (5598) and D (1.68) of PEW of the blank control, respectively (Table 4).

Table 3 Impurity analysis by XRF of the PEW before and after the extraction

<table>
<thead>
<tr>
<th>Sample</th>
<th>MgO</th>
<th>Al_{2}O_{3}</th>
<th>SiO_{2}</th>
<th>P_{2}O_{5}</th>
<th>SO_{3}</th>
<th>K_{2}O</th>
<th>Fe_{2}O_{3}</th>
<th>Na_{2}O</th>
<th>CaO</th>
<th>ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.000</td>
<td>0.088</td>
<td>0.533</td>
<td>0.045</td>
<td>0.043</td>
<td>0.000</td>
<td>0.000</td>
<td>0.004</td>
<td>0.240</td>
<td>0.031</td>
</tr>
<tr>
<td>Sand</td>
<td>0.004</td>
<td>0.034</td>
<td>0.730</td>
<td>0.017</td>
<td>0.060</td>
<td>0.018</td>
<td>0.045</td>
<td>0.021</td>
<td>0.113</td>
<td>0.000</td>
</tr>
<tr>
<td>Clay</td>
<td>0.000</td>
<td>0.039</td>
<td>0.318</td>
<td>0.015</td>
<td>0.036</td>
<td>0.025</td>
<td>0.027</td>
<td>0.014</td>
<td>0.065</td>
<td>0.000</td>
</tr>
<tr>
<td>Loam</td>
<td>0.004</td>
<td>0.036</td>
<td>0.495</td>
<td>0.012</td>
<td>0.000</td>
<td>0.022</td>
<td>0.082</td>
<td>0.026</td>
<td>0.177</td>
<td>0.000</td>
</tr>
</tbody>
</table>

Fig. 4 FT-IR spectra of PEW before and after reflux extraction of: a. blank; b. sand; c. clay; and d. loam samples.
4 Conclusions

We presented a method to recover PEW residues from soil using decalin solvent for reflux extraction. Both extraction frequency and extraction time have significant effects on the recovery of PEW, but the soil type used has little effect. The recovery of PEW samples was approximately 96.5% after three extractions at 90 °C for 60 min for all three types of soil. The FT-IR spectra and HT-GPC analysis show that there are no significant changes in chemical structures, molecular mass, as well as molecular mass distribution before and after the extraction. In addition, EA and XFR analysis indicate that the reflux extraction is specific for PEW in soil and do not introduce other impurities of significant amounts. Our results demonstrate that this procedure is effective and practical for extracting PEW residues from soil. This analytical method can potentially serve as a new approach in evaluating the degradation of PEW residues in soil over different period of time.

Acknowledgement

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References


