Advantage of solvothermal procedure for polychlorinated biphenyls removal from e-waste contaminated site

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1. Introduction

Aged soil contaminated by polychlorinated biphenyls (PCBs) has mainly resulted from inappropriate disposal of waste electrical and electronic equipment (WEEE) such as electric power capacitors and transformers [1–3]. This is especially true in China due to the previous existence of randomly disassembling electrical installations in WEEE dismantling area. Take Taizhou alone for example, which was the world centre for recycling capacitors and transformers, the area involved in crude dismantlement is about 300 km² [1]. Moreover, approximately 9000 tons of PCBs were produced and used primarily in capacitors for China before production of PCBs was banned in 1974 [4]. Long time storage of these outdated PCB-containing electrical installations has also led to the severe leakage of PCBs into the surrounding soil [5]. Due to the harmful effect of PCBs on humans and ecosystems, treatment of soil contaminated by PCBs has been a challenging task for decades.

Various technologies, including land burial, microbial degradation, solvent extraction, thermal desorption and incineration, have been developed for removal and disposal of PCBs from soil [6,7]. Among these technologies, an in situ capping approach using activated carbon and reactive metal particles has been extensively studied due to its less invasive nature [8–10]. This approach is a surface mediated process and adsorption of PCBs onto the surface plays an important role in the whole process [11]. But it is noteworthy that, a portion of PCBs was prone to be associated with soil organic matter such as humic acid (HA), bound humic acid (bound HA) [12,13] and thus result in the formation of unextractable (bound) PCBs [14,15]. Accordingly, these bound PCBs were difficult to be effectively disposed by capping approach [11,16].

Therefore, transferring PCBs from soil to the solvent and destroy PCBs through a secondary treatment is a simple and practicable technique [17,18]. Conventional extraction processes such as Soxhlet and elution also showed that a significant amount of PCBs introduced into a soil or sediment was unextractable by these classical extraction methods [12,16]. Previous studies implied that the longer a spiked contaminant was allowed to interact with the matrix, the higher unextractable fraction became [19–21]. In addition, freshly spiked pollutants can often be removed using relatively mild conditions, whereas quantitative removal of aged pollutants often requires higher temperature [6] and longer time as confirmed by supercritical fluid extraction. But as for supercritical fluid
extraction, it was observed that the high temperature and pressure resulted in chemical alteration of the extracted pollutants in some instances [22]. An alternative approach may be explored to use solvothermal process [23], which is usually conducted at lower temperature and pressure in comparison with supercritical fluid extraction. To our knowledge, only limited works focused on the application of this procedure for cleaning up organic pollutants [24].

The primary objective of this study was to evaluate the effectiveness of solvothermal procedure for removal of PCBs in aged contaminated soil. Effects of various treatment conditions on PCBs removal efficiency were evaluated, and a suitable solvothermal procedure for soil treatment was established.

2. Experimental

2.1. Chemical agents

HPLC grade acetone, hexane, methanol and isopropanol were purchased from J&K Chemical Ltd., USA. Florisil (60–100 mesh), copper powder (200 mesh), anhydrous sodium sulfate (Na2SO4), concentrated sulfuric acid (H2SO4), sodium hydroxide (NaOH), hydrochloric acid (HCl), and methyl isobutyl ketone (MIBK) were analytical reagents from domestic manufacturers. Standards of Aroclor 1242, Aroclor 1260 and PCB209 were obtained from Accu-Standard Inc., USA. Capacitor and transformer oil were obtained from domestic capacitors and transformers, and dissolved in hexane to prepare a stock solution of 18 mg/L and 60 mg/L, respectively.

2.2. Soils

Aged soil contaminated by PCBs in capacitor and transformer oil was obtained from WEEE recycling site in southeastern China. An uncontaminated soil was also collected and subjected to treatment for comparison. Soil samples were air-dried, finel ground and homogenized by sieving through a stainless steel 80 mesh sieve.

Freshly spiked PCB-contaminated soil samples were prepared as follows: triplicate sets of 1.0 g (for solvothermal process), 10.0 g (for Soxhlet extraction), and 10.0 g (for elution method) uncontaminated soil samples were placed into individual Erlenmeyer flasks, spiked with 1 mL stock solution, and saturated with hexane to ensure that the samples were homogenous. The flasks were placed in a hood and the solvents were allowed to evaporate.

2.3. Experimental procedures

In the Soxhlet system, about 10.0 g weighed soil was placed in the extraction thimble and extracted with 150 mL hexane/acetone (1:1, v/v) for 24 h.

A series of reactors consisted of 100 mL Teflon interiors and stainless exteriors were employed for the solvothermal experiments. In a typical run, a certain amount of organic solvent and weighed soil was introduced into a reactor and sealed. Then the reactor was placed into an oven, and the reactor temperature was raised to the desired temperature and held for a specified time. On the termination of the reaction, the mixture was separated by centrifugation (10,000 × g, 10 min, TG16-WS, China). Then the solvent phase was subjected to clean-up procedure and the solid phase was allowed to air-dry overnight. Among this part, solvents of hexane/acetone, methanol, isopropanol were examined to compare their solvothermal removal efficiency. Afterwards, the temperature varied from 90 °C to 170 °C at constant time and liquid to solid ratio, the treating time varied from 1 h to 15 h at constant temperature and liquid to solid ratio, and the liquid to solid ratio varied from 5:1 to 20:1 (mL/g) at constant temperature and time were performed to optimize the parameters of solvothermal process.

Fractionated analysis of PCBs was determined using the method officially accepted [25] and described in Nieman et al. [26]. The fraction of “extractable PCBs” was obtained by Soxhlet extraction. And the Soxhlet unextractable PCBs were referred to “bound PCBs”. In this study, aged soil samples were also subjected to sequential Soxhlet–solvothermal process for possible removal of bound PCBs, which meant that aged soil was extracted by Soxhlet initially and followed by solvothermal process.

In order to investigate the removal efficiency of extractable PCBs, solvothermal process using freshly spiked soil was also carried out and compared with the results of conventional Soxhlet extraction and elution method. As for the elution process, a small column apparatus (400 mm × 16 mm ID) was used. The column with a polytetrafluoroethylene stopcock was packed from the bottom up with a small pad of glass wool, 1 cm quartz sand, 6 cm soil and 1 cm quartz sand. A typical test involved 10.0 g soil and approximately 150 mL hexane/acetone (1:1, v/v). The solvent phase was sampled after it dripped off the column at ambient temperature and pressure.

Soil was fractionated by using MIBK method to evaluate the distribution of bound PCBs among soil fractions [26,27]. In this section, 10.0 g aged soil samples were separated into fulvic acid (FA), humic acid (HA), bound humic acid (bound HA), bound lipids and insoluble mineral components after extractable PCBs were removed by Soxhlet extraction. After separation, the residual mineral material in all fractions were collected from liquid phase by centrifugation (10,000 × g, 10 min) and combined together. FA, HA, bound HA and bound lipids in liquid phase were concentrated to small volume below 50 °C by a vacuum rotary evaporator (RE-52AA, Yarong, China). Then the obtained FA, HA, bound HA, bound lipids and well mixed mineral were respectively subjected to solvothermal procedure with 15 mL isopropanol.

Furthermore, the properties of aged soil before and after solvothermal treatment were analyzed. Moisture contents were determined gravimetrically on air-dry soil (105 °C, overnight). Soil pH values were determined with a pH meter (pHS-3C, Leici, China) in a liquid to solid ratio of 2.5:1 (mL/g) suspension in H2O. Soil organic matter was determined by spectrophotometry [28].

2.4. Clean-up procedures

The solvent phases were first evaporated on the vacuum rotary evaporator for solvent substitution with hexane. The extracts were then subjected to sulfuric acid cleanup and sulfur removal with copper powder. Subsequently, the collected fractions were transferred to a multilayer column, packed from the bottom up with 1 cm sodium sulfate, 5 cm Florisil and 1 cm sodium sulfate, and eluted with 100 mL hexane. After concentrated, the elutes were transferred to Kuderna–Danish (K–D) concentrators and evaporated to 1 mL under a stream of nitrogen flow for gas chromatography–mass (GC/MS) analysis.

2.5. PCBs analysis

Analysis of PCBs was accomplished by an Agilent 7890A gas chromatograph (GC) equipped with an Agilent 5975 C mass spectrometry detector and a HP-5 capillary column (USA). High purity He was used as carrier gas with a flow rate of 1 mL/min. The column temperature of chromatographic analysis was programmed as follows: the initial temperature was at 50 °C, and then increased to 150 °C at 20 °C/min, increased to 180 °C at 10 °C/min, finally increased to 280 °C at 3 °C/min and held for 2 min.
2.6. Quality control

The recovery of added PCB209 in the solvothermal procedure and Soxhlet extraction were in the range of 80–105%, which are acceptable for accurate quantification. Procedure blanks were run to determine background levels. PCBs were not detected in blank tests for Soxhlet extraction. Blank levels for the solvothermal procedure were typically ≤3% of the concentrations of PCBs in the samples. The presented concentrations were corrected accordingly. Statistical analysis of the results was performed in SPSS 19.0 (SPSS Inc., USA) using independent-samples t-test (p < 0.05).

Each experiment was carried out in triplicate for parallel test, and average values with standard errors were reported.

3. Results and discussion

3.1. Characterization of PCB species in the aged soil

The chromatogram of aged soil reveals almost 50 peaks, most of which are tri-CBs, tetra-CBs, hexa-CBs and hepta-CBs (Fig. 1). A comparison of the chromatograms of the soil sample and standard samples Aroclor 1242 and 1260 showed that these PCBs were identical as a mixture of Aroclor 1242 and 1260, which allowed us to use Aroclor 1242 and 1260 as standards to quantify PCBs in the soil based on EPA method 8082 [29] and previous literatures [30,31].

Each five major and well-resolved peaks of Aroclor 1242 and 1260 were chosen for quantification and labeled by the roman symbols in Fig. 1 since they represent the majority and provide accurate quantification results as suggested by Yak et al. [32]. These peaks were attributed to congeners of PCB18, PCB28, PCB44, PCB66, PCB118, PCB153, PCB138, PCB180, PCB170 in order.

3.2. Predominance of solvothermal process

The above experiments showed that solvothermal process could remove all PCB congeners attributed to Aroclor 1242 and Aroclor 1260 from aged soil, and high concentrations of ∑I-IV PCBs (sum of PCB8, PCB18, PCB28, PCB44, PCB66) and ∑IV-X PCBs (sum of PCB118, PCB153, PCB138, PCB180, PCB170) were removed by solvothermal procedure. However, the extraction amounts of those by Soxhlet were much less for ∑I-IV PCBs and undetectable for congeners belonged to Aroclor 1260. This reveals that solvothermal removal amounts were considerably higher than those with Soxhlet (p < 0.05).

Sequential Soxhlet–solvothermal process showed that solvothermal procedure after Soxhlet removed great amounts of PCB congeners from aged soil samples, e.g., 11.89 mg/kg of PCB8 was removed with hexane/acetone as a solvent (Table 1). As is known, bound residues are defined as parents or metabolites of contaminants left in sample after the sample was extracted by Soxhlet for 24 h [14,15,25]. Khan and Hamilton [33] demonstrated that a steady decrease of extractable prometryn was accompanied by a corresponding increase of bound residues. And 57.4% of application of prometryn resulted in the formation of bound residue in organic soil after 1 year of incubation time [22]. Similarly, as PCBs unextractable by Soxhlet are regarded as bound PCBs [12,13,16], the results shown in Table 1 confirmed the significant existence of bound PCBs in aged soil and the feasibility of solvothermal procedure to remove these PCBs.

As reported by previous studies [34–36], bound residues in soil can be mineralized, re-incorporated into humus, or released into soil solution by the actions of microorganisms, which result in their uptake by plants, biotic community or leakage into ground water and subsequently have impact not only on non-target animals or plants, but also human health via food-chains. Therefore, removal of bound PCBs is of great importance for safety reclamation of soil.

As for removal of extractable PCBs, Fig. 2 summarizes the comparison results of Soxhlet extraction, elution method and solvothermal procedure for freshly spiked soil. As can be seen, the removal efficiency of ∑I-IV PCBs and ∑IV-X PCBs by solvothermal procedure was almost the same with Soxhlet extraction (p = 0.091), but better than that of elution method (p = 0.074), which means that solvothermal procedure and Soxhlet extraction are equally effective.
effective in removing extractable PCBs from soil. Furthermore, solvothermal procedure is superior to Soxhlet extraction and elution method in point of using less solvent and time.

Obviously, as a practical technique to remedy contaminated soil, solvothermal procedure must not significantly affect soil properties [37]. As shown in Table 2, soil moisture was slightly lower than the original soil after solvothermal treatment. And the highest moisture content of soil after Soxhlet extraction was due to residual solvent on soil surface. Furthermore, solvothermal procedure slightly facilitated the change of soil acidity in point of the increase of pH value after solvothermal treatment. As for soil organic matter, it basically kept constant in a certain range before and after the treatment, which means that soil fertility was maintained after solvothermal procedure. This is consistent with previous reports [20,37], which suggest that supercritical fluid extraction with pure CO₂ at 150 °C and 1 h does not affect the bulk organic content of sediments.

Since organic pollutants, including PCBs, pesticides, and polycyclic aromatic hydrocarbon (PAH), display similar properties especially nature of binding to soil, it is indisputable that solvothermal procedure should own the infinite superiority in treating soil contaminated by all organic pollutants.

3.3. Solvothermal extraction mechanisms

Similar to the process of supercritical fluid extraction [20], the superior removal performance of solvothermal procedure was attributed to the enhanced temperature and slightly higher pressure as compared to Soxhlet extraction and elution method. Although PCBs are insoluble under ambient atmosphere and temperature, bound PCBs were quickly dissolved by organic solvent in the sealed pressure vessel at the increased temperature. The role of pressure was important in that a slight higher pressure keeps the solvent in the liquid phase at a high temperature as described by Gan et al. [38] for accelerated solvent extraction.

According to previous reports [12,13], bound PCBs were partitioned into different components of soil. The distribution of bound PCBs among five soil fractions was thus evaluated to understand the fate of bound PCBs in real aged soil. Fig. 3 shows that 40.83% (∑I-PCBs) and 38.04% (∑III-XPCBs) of selected PCB congeners exist in HA of contaminated soil, while 28.37% (∑IV-PCBs) and 25.60% (∑V-XPCBs) are associated with bound HA, and the remaining are associated with bound lipids, mineral and FA in descending order. As for important components of humin, bound HA, bound lipids and mineral accounted for more than 60% of selected PCB congeners. Kohl and Rice [13] indicated that at least 50% of bound PCBs are associated with humin due to the strong adsorption capacity of organic carbon. Further divisions of humin by MIBK partitioning shows that bound HA and bound lipids also have a high affinity for PCBs. In addition, it should be noted that a certain amount (>10%) of PCBs was associated with the insoluble mineral component although this material is essentially inorganic and contains much less organic matter by weight. This distribution of bound PCBs in different soil fractions was relevant to chemical characterization of these fractions and how they react with PCBs [13].

3.4. Optimization of the solvothermal procedure

As can be seen from Table 1, all of the selected solvents achieved high PCBs removal efficiency. Hexane/acetone was better than

### Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>Hexane/acetone (1:1)</th>
<th>RSD (%)</th>
<th>Methanol</th>
<th>RSD (%)</th>
<th>Isopropanol</th>
<th>RSD (%)</th>
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<tbody>
<tr>
<td>PCB-8</td>
<td></td>
<td>11.89</td>
<td>1.1</td>
<td>7.55</td>
<td>0.4</td>
<td>14.76</td>
<td>1.96</td>
</tr>
<tr>
<td>PCB-18</td>
<td></td>
<td>34.30</td>
<td>9.3</td>
<td>18.56</td>
<td>2.9</td>
<td>38.13</td>
<td>5.66</td>
</tr>
<tr>
<td>PCB-28</td>
<td></td>
<td>37.69</td>
<td>8.1</td>
<td>25.86</td>
<td>3.4</td>
<td>43.47</td>
<td>7.48</td>
</tr>
<tr>
<td>PCB-44</td>
<td></td>
<td>10.84</td>
<td>3.2</td>
<td>6.52</td>
<td>4.3</td>
<td>10.79</td>
<td>4.82</td>
</tr>
<tr>
<td>PCB-66</td>
<td></td>
<td>30.82</td>
<td>12.8</td>
<td>35.29</td>
<td>2.7</td>
<td>44.43</td>
<td>4.98</td>
</tr>
<tr>
<td>PCB-118</td>
<td></td>
<td>66.63</td>
<td>13.5</td>
<td>93.99</td>
<td>11.8</td>
<td>107.45</td>
<td>22.78</td>
</tr>
<tr>
<td>PCB-153</td>
<td></td>
<td>112.70</td>
<td>20.1</td>
<td>159.71</td>
<td>10.2</td>
<td>176.98</td>
<td>16.5</td>
</tr>
<tr>
<td>PCB-138</td>
<td></td>
<td>84.24</td>
<td>9.8</td>
<td>120.39</td>
<td>12.2</td>
<td>135.49</td>
<td>13.14</td>
</tr>
<tr>
<td>PCB-180</td>
<td></td>
<td>96.30</td>
<td>8.3</td>
<td>120.19</td>
<td>15.3</td>
<td>138.61</td>
<td>10.26</td>
</tr>
<tr>
<td>PCB-170</td>
<td></td>
<td>29.32</td>
<td>6.2</td>
<td>36.72</td>
<td>3.0</td>
<td>44.20</td>
<td>9.21</td>
</tr>
<tr>
<td>∑I-PCBs</td>
<td></td>
<td>125.54</td>
<td>23.4</td>
<td>93.78</td>
<td>16.2</td>
<td>151.58</td>
<td>15.6</td>
</tr>
<tr>
<td>∑III-XPCBs</td>
<td></td>
<td>389.19</td>
<td>10.5</td>
<td>531.00</td>
<td>14.9</td>
<td>602.73</td>
<td>21.9</td>
</tr>
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</table>

*The samples were pre-extracted by Soxhlet procedure. Concentrations are given as mg/kg of dry weight. Temperature and time are 150 °C and 10 h.*

### Table 2

<table>
<thead>
<tr>
<th>Soil</th>
<th>Air-dry soil moisture content (g/kg)</th>
<th>pH (2.5:1)</th>
<th>Organic matter (g/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original soil</td>
<td>13.54</td>
<td>5.00</td>
<td>36.42</td>
</tr>
<tr>
<td>Soil after Soxhlet extraction</td>
<td>20.92</td>
<td>4.88</td>
<td>36.75</td>
</tr>
<tr>
<td>Soil after solvothermal procedure</td>
<td>12.90</td>
<td>5.17</td>
<td>35.77</td>
</tr>
</tbody>
</table>

*Temperature and time are 150 °C and 10 h. Solvent is isopropanol.*

![Fig. 3. Distribution of bound PCBs in different soil fractions. Solvothermal conditions: temperature 150 °C; time 10h; liquid to solid ratio 15:1; solvent isopropanol.](image-url)
methanol for congeners of PCB8, PCB18, PCB28 and PCB44 in removing bound PCBs. But as for PCB66, PCB118, PCB153, PCB138, PCB180 and PCB170, it was contrary. This different trend was attributed to the different polarities of these congeners and solvents [38]. Furthermore, isopropanol showed its superiority over hexane/acetone and methanol in all cases. Hence isopropanol is considered as superior solvent in this study. Accordingly, it is necessary to determine optimal solvent for maximum recoveries before using solvothermal procedure as also demonstrated by Bandh et al. for accelerated solvent extraction [19].

Fig. 4 shows that PCBs removal efficiency was not obvious at lower temperatures (90–110 °C), and it continuously increased till around 150 °C, but declined at higher temperature 170 °C for congeners of PCB66, PCB118, PCB153, PCB138, PCB180 and PCB170. This implied that desorption of PCBs from sample matrix controls the removal efficiency [39] and certain intermolecular bonds between PCBs and soil matrix can only be broken at higher temperatures and pressures, and this is probably the decisive advantage of solvothermal procedure as compared to Soxhlet or elution [40]. However, certain temperature range (>150 °C) may limit the removal efficiency, as also demonstrated by Hubert et al. [40]. In contrast, concentrations of PCB8, PCB18, PCB28 and PCB44 kept increase from 90 °C to 170 °C. The difference in optimal temperatures for PCB congeners was ascribed to the different chlorination degree of PCB congeners as discussed by Björklund et al. [20]. Langenfeld et al. [39] also stated that higher molecular weight PCB congeners were more efficiently extracted than low molecular weight congeners because the low molecular weight PCB congeners are more tightly bound to the matrix. Therefore, the completely removal of low molecular weight congeners only can be achieved at higher temperature.

As demonstrated in Fig. 5, the removal efficiency increased as the prolonging of time till about 10 h for all of selected PCBs. But after 10 h, concentrations of selected PCB congeners declined slightly. It also should be noted that, concentrations of PCB8, PCB18, PCB28, PCB44 and PCB66 were flat initially and then decreased as the increase of liquid to solid ratio (Fig. 6). This was mainly ascribed to the pressures in the sealed reactors, which varied with the amounts of solvent. As for PCB118, PCB153, PCB138, PCB180 and PCB170, those concentrations continued to grow and then reached a plateau. The remarkable difference in changing trends was relevant to the amounts of PCB congeners in the contaminated soil in respect that solubility of the contaminant will determine the partitioning equilibria between the solvent and the sample matrix [39].

The above results are in accordance with previous findings [20,39,41], which suggested that the soil matrix was most important in controlling desorption behavior and the extraction amount of contaminant was a function of its molecular weight, its
concentration and length of time for extraction as discussed for supercritical fluid extraction.

4. Conclusions

This study demonstrated that solvolithic process was a practical and efficient method for the treatment of long-term contaminated site by PCBs. In the soil of this type of site, bound PCBs were partitioned into different components of soil organic matter, i.e., approximately 40% of bound PCBs were associated with HA, followed by bound HA, bound lipids, mineral, and FA. The most effective solvent for the solvolithic process was isopropanol. The optimum performing temperature, time and liquid to solid ratio for PCB8, PCB18, PCB28, PCB44, and PCB66 were 170 °C, 1 h and 10:1, respectively. As for higher molecular weight PCB congeners, these conditions were 150 °C, 10 h and 15:1. Furthermore, the soil fertility was maintained after the solvolithic process. Therefore, it is possible for the reclamation of the contaminated site after the treatment.

Acknowledgements

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References


