Application of microwave-irradiated manganese dioxide in the removal of polychlorinated biphenyls from soil contaminated by capacitor oil

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The removal of polychlorinated biphenyls (PCBs) from soil contaminated with capacitor oil, using microwave (MW)-irradiated manganese dioxide (MnO\textsubscript{2}), was examined under different conditions. The effects of different types of MnO\textsubscript{2} added as oxidant, as well as the initial amount of water, MnO\textsubscript{2}, and sulphuric acid solution, were also investigated. The removal efficiencies for dichlorobiphenyls, trichlorobiphenyls, tetrachlorobiphenyls, pentachlorobiphenyls, hexachlorobiphenyls, heptachlorobiphenyls, and octachlorobiphenyls were approximately 95.9\%, 82.5\%, 52.0\%, 71.6\% 62.5\%, 28.6\%, and 16.1\%, respectively, by 800 W MW irradiation for 45 min with the assistance of 0.1 g δ-MnO\textsubscript{2} and 0.2 mL water in 1.0 g severely PCB-contaminated soil ($\sum$ PCB = 1560.82 mg/kg); meanwhile, the concentrations of Mn$^{2+}$ ions detected were from 10.6 ± 1.9 mg/kg at 0 min to 108.2 ± 7.8 mg/kg after 45 min MW irradiation, indicating that MnO\textsubscript{2} acted as not only a MW absorber but also an oxidizer. Removal efficiencies of PCBs from contaminated soil increased with increasing the amounts of water and MnO\textsubscript{2} added. The type of MnO\textsubscript{2} also affected the removal of PCBs, following an order of δ-MnO\textsubscript{2} > α-MnO\textsubscript{2} > β-MnO\textsubscript{2}. The addition of low concentration of sulphuric acid (such as 1.0 mol/L) solution was favourable for the removal of low chloro-substituted PCBs, but the addition of more than 1.0 mol/L sulphuric acid reduced the removal of all PCBs. The pronounced removal of PCBs from contaminated soil in a short treatment time indicates that MW irradiation with the assistance of MnO\textsubscript{2} is an efficient and promising technology for the remediation of PCB-contaminated soil.

**Keywords:** microwave irradiation; polychlorinated biphenyls; manganese dioxide; soil remediation

1. Introduction

Polychlorinated biphenyls (PCBs) are persistent organic pollutants that threaten the environment and human health [1]. In China, approximately 10,000 tons of PCBs were produced from 1965 to 1974 (the production of PCBs was banned in 1974). Furthermore, China imported numerous capacitors containing PCBs from Belgium and France [2]. These PCBs can be released from commercial PCB-containing products and enter the environment via waste emissions, oil leakage, volatilization, dry and wet deposition, or other means, thus resulting in widespread environmental pollution. A large amount of disused capacitors and transformers could lead to serious leakage of PCBs because of their improper disposal, which would pose a great risk to the environment and human health [3]. Incineration was generally used to treat PCB-contaminated soils at Superfund sites in the USA; however, there was widespread public opposition to this approach owing to the potential for release of dioxin via the flue gas stream [4]. Therefore, it is very important to find other safe and efficient technologies for the treatment of PCB-containing wastes.

Microwave (MW) energy induces molecular motion by rotation of dipoles and migration of ions; materials that absorb MW irradiation are called dielectrics [5]. MW heating has been widely used in organic and inorganic synthesis, dehydration, food sterilization, extraction and environmental engineering because of its rapid, uniform and selective advantages [6–9]. In the remediation of contaminated soils, MW could achieve a fast removal of pollutants whether the soils are permeable or not [5,10]. Abramovitch et al. [11] used MW energy to decompose chlorinated aromatic compounds in soil with the assistance of microwave absorbents (powdered Cu$_2$O, Al, graphite, or pencil lead) and NaOH. Highly efficient decomposition was achieved by the addition of powdered Cu$_2$O or Al and NaOH. Only minute amounts of decomposition products could be extracted from the soil following remediation, suggesting that the majority of the compounds were probably mineralized or very tightly bound to the soil. Liu et al. [12–14] reported the application of microwaves in combination with activated carbon for the removal of pentachlorophenol and PCBs. It is well known that MnO\textsubscript{2} was not only one of the most important natural oxidants in soils [15,16], but also one of the strongest MW absorbers [17,18]. MnO\textsubscript{2} has been shown to be an effective oxidant for a wide range of pollutants including substituted phenols and anilines.

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[19,20]. Furthermore, Pizzigallo et al. [21] reported that MnO$_2$ alone could partially remove five PCBs from soil. Under the combined effects of MW irradiation and MnO$_2$, a complete removal of hexachlorobenzene from soil was obtained within 10 min by the addition of H$_2$SO$_4$, but no significant removal was observed by the addition of NaOH or H$_2$O in the same conditions [5]. In our previous work [22], PCB28, PCB77, and PCB118 were chosen as representatives of PCBs to investigate removal efficiencies of PCB using microwave-irradiated $\delta$-MnO$_2$ in two types of soils (Ali-Perudic Ferrosols and Udic Argosols), and their removal efficiencies were found to be above 95%. However, the feasibility of this technology for the removal of PCBs with remarkably high concentrations in soil heavily contaminated by capacitor oil has not been well documented. Therefore, on the basis of our previous work, the purpose of this study was to further investigate the removal efficiencies for dozens of PCB congeners containing different chlorine substituent numbers in actual heavily PCB-contaminated soil collected from Zhejiang province in China and to discuss the effects of MW irradiation time, the initial amounts of H$_2$O and MnO$_2$, type of MnO$_2$, and acidic conditions on the removal of dozens of PCBs.

2. Experimental

2.1. Materials

Soil heavily contaminated by capacitor oil was collected from a transformer-filled landfill in Ningbo, Zhejiang Province, China. The soil was air-dried in a fume hood, and then ground and sieved through a 20 mesh sieve to remove debris and stones. The soil was then sealed in a glass bottle and used as needed.

PCB28 and a PCB congener mixture containing 32 standards were purchased from AccuStandard, USA. High-performance liquid chromatographic-grade n-hexane and acetone were obtained from Merck (Darmstadt, Germany). H$_2$SO$_4$ was obtained from Shanghai Chemical Factory (China). Ultra pure water was obtained using a Milli-Q Advantage A10 Water Purification System from Millipore (Bedford, MA, USA), and all the solutions used in this study were prepared with ultrapure water.

MnO$_2$ was synthesized according to the methods of Cai and Ren [23] and Wang and Li [24]. The preparation and characterization of synthesized MnO$_2$ are described in detail in the supplementary information (Sections 1 and 2). The synthesized MnO$_2$ was characterized as $\delta$-MnO$_2$, $\alpha$-MnO$_2$, and $\beta$-MnO$_2$ according to X-ray diffraction analysis. The Brunauer–Emmett–Teller (BET) specific surface of area of $\delta$-MnO$_2$, $\alpha$-MnO$_2$, and $\beta$-MnO$_2$ are 250.44, 23.45 and 50.20 m$^2$/g, respectively. Scanning electron microscopy images indicated that the synthesized $\delta$-MnO$_2$ was composed both of granular and rod-shaped microparticles (Figure S2a, supplementary information), but $\alpha$-MnO$_2$ and $\beta$-MnO$_2$ were composed of nanorods and nanowires, respectively (Figure S2b and S2c, Supplementary information).

2.2. Methods

The experimental apparatus was the same as that in our previous study [22]. In brief, a microwave oven with a frequency of 2450 MHz was used. The microwave apparatus had a continuous adjustable power setting, which could be set to a fixed power output, such as 800 W, based on the requirement of the experiment. For a given material, MW power is very important for the temperature attained by MW irradiation. Our previous study showed that higher MW power was more favourable for the removal of PCBs. In order to compare with previous work, all of the experiments were carried out at 800 W in this study. A 45 mL brown borosilicate glass bottle capped with a Teflon-lined septum (CNW, Germany) was used as a batch reactor.

Certain amounts of MnO$_2$ were added and mixed thoroughly by hand with 1.0 g of PCB-contaminated soil in a bottle. Then, different amounts of H$_2$O (0, 0.1, 0.2 and 0.3 mL) were introduced. The effect of MnO$_2$ amount on the PCB removal efficiencies was investigated with addition of 0, 0.01, 0.02 and 0.1 g of $\delta$-MnO$_2$ in 1.0 g of PCB-contaminated soil. Different concentrations of H$_2$SO$_4$ solution (0.2 mL), 1.0, 2.0 and 4.0 mol/L, were added to 1.0 g of PCB-contaminated soil to evaluate the influence of proton concentrations on the PCB removal efficiencies. After the cap was screwed on, the bottles were placed on the rotary table in a microwave oven, and each batch treatment was set up as four replicates. The samples were treated by microwave irradiation under different conditions. At the designated time (e.g. 0, 1, 4, 8, 15, 30 and 45 min), microwave irradiation was stopped, and the MW-treated soil samples were extracted by an ultrasonication method after the irradiated samples were cooled to room temperature. One gram samples of MW-treated and raw soil were individually extracted with 10 mL of acetone and hexane solvent mixture (1:1, v/v) for 30 min in a 30 °C ultrasonic water bath. Then, the samples were centrifuged at 4000 rpm for 10 min, and 0.1 mL of supernatant was drawn out using a micro-syringe and diluted to 2.0 mL with hexane for gas chromatography analysis.

To monitor the generation of Mn$^{2+}$ during the oxidative degradation of PCBs by MW-irradiated MnO$_2$, four replicates of 1.0 g of MW-treated soil samples with addition of 0.1 g of $\delta$-MnO$_2$ were measured for concentration of generated Mn$^{2+}$ after MW irradiation for 0, 4, 15 and 45 min. The procedure of extracting generated Mn$^{2+}$ from soil was based on the method of Lu [25]. In brief, 20.0 mL of Al$_2$(SO$_4$)$_3$ (0.1 mol/L, pH 2.5) was added to each of four soil samples and shaken on a mixer for 5 min. The mixture was filtered and 5.0 mL of the filtrate was immediately poured into a 25 mL colorimetric tube, followed by the addition of 1.6 mL of H$_2$SO$_4$ (1:1, v/v), 0.8 mL of H$_2$PO$_4$ (1.69 g/mL) and 8 mL of water. Then, 0.1 g of KIO$_4$ was added and
placed in a 90 °C water bath for 30 min until the solution had completely changed to a purple colour and no further colour change was observed. After cooling to room temperature, the Mn⁴⁺ in the solution was monitored using a Rayleigh UV-1600 UV-Vis spectrophotometer (Beijing, China). The absorbance of the solution was measured at 540 nm and the concentration was determined by the standard curve.

2.3. Analysis methods
Quantitative analysis of PCBs was accomplished by an Agilent 7890A gas chromatograph equipped with an electron capture detector, using external standards and the peak area calculation method. An Agilent 1901J-413 column with a capillary length of 30 m × 0.32 mm × 0.25 μm was used. A split–splitless injector in the splitless mode was used. The inject volume was 1 μL. The injector and detector temperature were set at 250 °C and 300 °C, respectively. N₂ was used as the carrier and make-up gas with a flow rate of 1.0 mL/min and 60.0 mL/min, respectively. The column temperature was programmed as follows: 150 °C hold for 2 min, 7 °C to 280 °C and 2 min hold.

3. Results and discussion
3.1. Residual characteristics of PCBs in raw contaminated soil
The raw soil in this study was severely contaminated by capacitor oil that had leaked from discarded transformers. The chromatogram of the raw soil without MW irradiation revealed about 35 peaks, most of which were 3-Cl, 4-Cl, and 5-Cl substituted congeners, as shown in Figure S3 (supplementary information). Such a great number of congeners made quantification extremely complicated and with large error bars. Therefore, only 18 major and well-resolved peaks were chosen from the chromatogram for quantification purposes, because these 18 peaks could represent the majority of PCBs and satisfy the requirements for quantification, as suggested by previous studies [13, 26]. These 18 major peaks included one dichlorobiphenyl (2,4′-DiCB, PCB8), two trichlorobiphenyls (2,2′,5-TriCB, PCB18; 2,4,4′-TriCB, PCB28), four tetrachlorobiphenyls (2,2′,3,5′-TetraCB, PCB44; 2,2′,5,5′-TetraCB, PCB52; 2,3′,4,4′-TetraCB, PCB66; 3,3′,4,4′-TetraCB, PCB77), four pentachlorobiphenyls (2,2′,4,5,5′-PentaCB, PCB101; 2,3′,3,4,4′-PentaCB, PCB105; 2,3,4,4′,5-PentaCB, PCB118; 3,3′,4,4′,5,5′-PentaCB, PCB126), three hexachlorobiphenyls (2,2′,3,3′,4,4′-HexaCB, PCB128; 2,2′,3,4,4′,5′-HexaCB, PCB137; 2,2′,4,4′,5,5′-HexaCB, PCB153), three heptachlorobiphenyls (2,2′,3,3′,4,4′,5-HeptaCB, PCB170; 2,2′,3,4,4′,5,5′-HeptaCB, PCB180; 2,2′,3,4,4′,5,6-HeptaCB, PCB187), and one octachlorobiphenyl (2,2′,3,3′,4,4′,5,6-OctaCB, PCB195). Direct comparison of the individual peak areas before and after MW irradiation was made by normalizing each peak area with the external standard.

Table 1 shows the concentrations of the 18 selected PCB congeners in the contaminated raw soil, and the total concentration of the 18 PCBs in the raw soil was about 1560.82 mg/kg. The homologue profile of PCBs in the raw soil was similar to the composition characteristics

| PCB congener | Retention time (min) | Concentrationa (mg/kg) | Per cent b (%) | Substituent number | Concentrationc (mg/kg) | Per cent d (%) |
|--------------|---------------------|------------------------|----------------|--------------------|------------------------|----------------|
| PCB8         | 9.14                | 131.51                 | 8.43           | 2-Cl               | 131.51                 | 8.43           |
| PCB 18       | 10.25               | 435.33                 | 27.89          | 3-Cl               | 882.62                 | 56.55          |
| PCB 28       | 11.42               | 447.29                 | 28.66          | 4-Cl               | 348.61                 | 22.34          |
| PCB 52       | 12.32               | 97.42                  | 6.24           | 5-Cl               | 29.58                  | 1.89           |
| PCB 44       | 12.87               | 65.33                  | 4.19           |                     |                        |                |
| PCB 66       | 13.78               | 163.90                 | 10.50          |                    |                        |                |
| PCB 77       | 14.57               | 21.97                  | 1.41           |                    |                        |                |
| PCB 101      | 13.98               | 104.76                 | 6.71           | 5-Cl               | 161.50                 | 10.35          |
| PCB 118      | 15.52               | 46.51                  | 2.98           |                    |                        |                |
| PCB 105      | 16.72               | 3.81                   | 0.24           |                    |                        |                |
| PCB 126      | 17.42               | 6.42                   | 0.41           |                    |                        |                |
| PCB 153      | 16.16               | 17.68                  | 1.13           | 6-Cl               | 29.58                  | 1.89           |
| PCB 138      | 16.84               | 10.83                  | 0.69           |                    |                        |                |
| PCB 128      | 17.84               | 1.07                   | 0.07           |                    |                        |                |
| PCB 187      | 17.63               | 1.06                   | 0.07           | 7-Cl               | 5.38                   | 0.34           |
| PCB 180      | 18.12               | 2.06                   | 0.13           |                    |                        |                |
| PCB 170      | 19.09               | 2.26                   | 0.14           |                    |                        |                |
| PCB 195      | 19.82               | 1.63                   | 0.10           | 8-Cl               | 1.63                   | 0.10           |
| ΣPCBs        | 1560.82             | 100                    |                |                    | 1560.82                | 100            |

a Concentration of each PCB congener.
b Per cent 1 = each PCB congener/ ΣPCBs × 100%.
c ΣPCBs with the same number of chloro-substituents.
d Per cent 2 = ΣPCBs with the same number of chloro-substituents/ ΣPCB × 100%.
of PCBs in Chinese transformer oil reported by Huang et al. [27]. The major homologues were TriCB (56.55%) followed by TetraCB (22.34%), PentacB (10.35%), and DiCB (8.43%). The concentration of PCB28 (447.29 mg/kg) was the highest in all congeners, followed by PCB18 with the concentration of 435.33 mg/kg. Some congeners with concentrations over 100 mg/kg were PCB8, PCB86, and PCB101. The concentrations of PCB52 and PCB44 were measured to be 97.42 and 65.33 mg/kg, respectively. The concentrations of these four dioxin-like PCBs (PCB77, PCB118, PCB 105, and PCB 126) in the raw soil were 21.97, 46.51, 3.81 and 6.42 mg/kg, respectively. The amounts of HexaCB, HeptaCB and OctaCB were quite low in the contaminated raw soil, which accounted for 1.89%, 0.34%, and 0.1% of \( \sum \) PCBs, respectively. Although the residuals of high chlorinated biphenyls in raw soil were found to be very low, the degradation rate of PCBs decreased as chlorine substitution increased, as summarized by Furukawa et al. [28]. Sinkkonen and Paasivirta [29] had reported an environmental half-life time of 10 years for PCB52, PCB77, PCB101, PCB10 and PCB126 in soil; however, the environmental half-life time of PCB138, PCB153, and PCB180 was estimated to be 18.8, 18.8 and 37.7 years, respectively, indicating that PCBs are very slow to degrade in soil, especially for high chlorinated biphenyls.

3.2. Removal efficiencies of PCBs using MW-irradiated \( \delta\)-MnO\(_2\)

Figure 1 illustrates that, of the four different treatments, MW-irradiated \( \delta\)-MnO\(_2\) in the presence of water resulted in highest PCB removal. Less than 20% of PCBs could be removed from soil when the contaminated soil was only treated by MW irradiation for 45 min in the absence of \( \text{H}_2\text{O}\) and MnO\(_2\), indicating that MW irradiation alone has weak efficiency for the removal of PCBs. MW irradiation with the assistance of \( \text{H}_2\text{O}\) slightly enhanced the removal efficiencies of low chlorinated biphenyls, but this treatment decreased the removal of high chlorinated biphenyls (Figure 1). The addition of water affects the final temperature of the reaction system during MW heating, because water has a high dielectric loss factor [30]. The removal of PCBs from soil by MW irradiation in the presence of \( \text{H}_2\text{O}\) might be partly accomplished through steam distillation, which would result in some of the PCBs desorbing out of the soil and having more chance to be decomposed, as observed in previous studies [13,31]. Thus, an enhancement of the removal efficiencies of low chlorinated biphenyls obtained with the addition of water might be attributed to the steam distillation effect owing to the relatively low steaming temperature of low chlorinated biphenyls. However, high chlorinated biphenyls, such as HexaCB, HeptaCB and OctaCB, were difficult to desorb and steam out from soil by MW heating, even when a higher final temperature of the reaction system was attained in the presence of water, because of their higher steaming temperatures and stronger affinities for soil.

Comparing to direct MW irradiation, the removal efficiencies of all PCBs were considerably improved by MW irradiation for 45 min with the assistance of 0.1 g of \( \delta\)-MnO\(_2\) (Figure 1), indicating that most PCBs were removed from soil through oxidative degradation by \( \delta\)-MnO\(_2\). The combination of 0.1 g \( \delta\)-MnO\(_2\) with 0.2 mL \( \text{H}_2\text{O}\) further increased the removal of PCBs by MW irradiation (Figure 1), especially for DiCB, TriCB, PentaCB and HexaCB. The removal efficiencies of DiCB and TriCB by MW irradiation in the presence of \( \delta\)-MnO\(_2\) and \( \text{H}_2\text{O}\) were high, up to 95.9% and 82.5%, respectively. However, the removal efficiencies of TetraCB, PentaCB, HexaCB, HeptaCB and OctaCB were about 52.0%, 71.6%, 62.5%, 28.6% and 16.1%, respectively, obviously lower than those of DiCB and TriCB. The higher the number of chlorine substituent, the lower the removal of PCBs observed in this study, as already reported in abiotic and biotic transformation of PCBs [21,32,33].

Both water and \( \delta\)-MnO\(_2\) are dielectrics that can absorb large amounts of MW energy. Therefore, when water and \( \delta\)-MnO\(_2\) were added, high temperature and high pressure occurred in the bottle during MW irradiation [5]. Many complex reactions should take place under such high temperature and high pressure conditions. Varanasi et al. [34] have reported that the destruction efficiencies of PCBs could be increased by increasing the water temperature when PCB-contaminated soil was mixed with iron nano-particles in water, which suggested that the thermal decomposition of PCBs would occur under MW irradiation in the presence of water and generate small molecule fragments that could be bound tightly to soil [35]. On the other hand, the oxidative degradation of PCBs by \( \delta\)-MnO\(_2\) at room temperature has also been confirmed by Pizzigallo et al. [21], which implied that a higher removal efficiency of PCBs would be achieved by MW-irradiated \( \delta\)-MnO\(_2\) under a higher temperature condition. Thus, both the thermal decomposition and the oxidative degradation contributed to the removal of PCBs under MW irradiation, but the oxidative degradation played a dominating role in removing PCBs based on Figure 1. Furthermore, the effects of irradiation time, the initial
amounts of added water and $\delta$-MnO$_2$, the type of MnO$_2$, and the acidity of the reaction system on the removal efficiencies of PCBs from actual contaminated soil were also examined and the details are presented in the following sections.

### 3.3. Effect of irradiation time

Figure 2 presents the removal efficiencies of PCBs from 1.0 g of actual heavily contaminated soil after four different MW irradiation times (4, 8, 15 and 45 min) in the presence of 0.1 g $\delta$-MnO$_2$ and 0.2 mL water. The removal efficiencies of all selected PCBs were found to increase with increasing irradiation time, although in a nonlinear fashion. For example, the removal efficiency of DiCB was observed to be approximately 50.2%, 86.2%, 95.0% and 95.9% after irradiation for 4, 8, 15 and 45 min, respectively, indicating that DiCB is highly susceptible to oxidation by MW-irradiated $\delta$-MnO$_2$. Likewise, the removal efficiencies of TriCB, TetraCB, PentaCB and HexaCB were considerably enhanced when irradiated from 4 min to 15 min, and then slightly increased when irradiated in the range of 15–45 min. On the other hand, the removal efficiencies of HeptaCB and OctaCB exhibited a slow increase when irradiated from 4 min to 45 min. Based on the report of Pizzigallo et al. [21], the mechanochemical complete removal of 2,2'-DiCB and a removal of 30% and 20% of 2',3,4-TriCB and 3,3',4,4'-TetraCB by $\delta$-MnO$_2$ needed 10 days and 90 days, respectively; however, the removal of 95.9%, 82.5%, and 52.0% of 2,4'-DiCB, TriCB and TetraCB was achieved in only 45 min by MW-irradiated $\delta$-MnO$_2$. The great reduction in treatment time in this study demonstrates that MW irradiation with the assistance of MnO$_2$ is an efficient and promising treatment technology for the remediation of heavily PCB-contaminated soil.

### 3.4. Effect of water content

Water is a typical polar substance that can greatly absorb MW energy. Additionally, changes in water content will alter the conductivity and permittivity of the treated soil [14]. Therefore, water content is an important factor that may influence the removal of PCBs by MW-irradiated MnO$_2$. Four amounts of water (0, 0.1, 0.2 and 0.3 mL) were added to 1.0 g of soil with 0.1 g of $\delta$-MnO$_2$ and treated with MW irradiation for 45 min to evaluate the influence of water content on the removal of PCBs from soil, and the results are presented in Figure 3. When no water was added, the removal efficiencies of PCBs slightly increased as the addition of water was increased to 20% of treated soil mass (0.2 mL water). Little difference was observed between the addition of 0.2 mL (20%) and 0.3 mL (30%) water, suggesting that excess water may not favour the temperature increase in the reaction system, because the circles of evaporation and condensation of water may consume the energy of the reaction system [13]. Thus, the optimal water content should be 20% of treated soil mass.

### 3.5. Effect of $\delta$-MnO$_2$ dosage

The removal efficiencies of PCBs from 1.0 g of contaminated soil with the addition of 0.01 g, 0.02 g and 0.1 g of $\delta$-MnO$_2$ in the presence of 0.2 mL of water are shown in Figure 4a. It is evident from Figure 4a that the removal of PCBs increased with the added amount of MnO$_2$. When no $\delta$-MnO$_2$ was added, the removal efficiencies of PCBs ranged from 2.56% for HeptaCB to 26.71% for DiCB (Figure 4a). When 0.01 g and 0.02 g of $\delta$-MnO$_2$ were added, the removal efficiencies of PCBs were increased to a range of 5.17–39.70% and 8.87–44.82%, respectively. When the added amount of $\delta$-MnO$_2$ was up to 0.1 g, the removal efficiencies of DiCB, TriCB, TetraCB, PentaCB, HexaCB, HeptaCB and OctaCB reached 95.9%, 82.5%, 52.0%, 71.6%, 62.5%, 28.6% and 16.1%, respectively.
Figure 4. Effect of MnO$_2$ dosage on the removal efficiencies of PCBs from 1.0 g heavily contaminated soil (a) and the generated concentration of Mn$^{2+}$ in the presence of 0.1 δ-MnO$_2$ (b) by 800 W MW irradiation for 45 min with the addition of 0.2 mL water.

Accordingly, the concentration of Mn$^{2+}$ was detected to be 10.6 ± 1.9 (representing the background value of free Mn$^{2+}$ in the treated soil), 29.6 ± 1.1, 62.7 ± 3.6 and 108.2 ± 7.8 mg/kg for 0, 4, 15 and 45 min of MW irradiation in the presence of 0.1 g δ-MnO$_2$ (Figure 4b). The generation of Mn$^{2+}$ ions from δ-MnO$_2$ increased with increasing removal of PCBs, indicating that δ-MnO$_2$ oxidized PCBs leading to its reduction into Mn$^{2+}$ ions. On the other hand, Guan et al. [17] reported that MnO$_2$ is a strong microwave absorbent with a very broad bandwidth, and its temperature could increase from 298 to 1378 K in 100 s at a speed of 10.80 K/s when subjected to electromagnetic wave irradiation. Such a high temperature on the surface of δ-MnO$_2$ will accelerate the oxidative removal of PCBs from soil. Thus, an increase in the initial amount of MnO$_2$ added can lead to the absorption of more microwave energy, effectively enhancing MnO$_2$ reactivity and oxidizing more PCBs.

3.6. Effect of MnO$_2$ type

Different types of MnO$_2$, such as α-MnO$_2$, β-MnO$_2$, and δ-MnO$_2$, exhibited remarkable discrepancies in oxidation capacity and morphology [32]. Duan et al. [18] also found that different crystalline types of MnO$_2$ have different electromagnetic characteristics. To examine the effect of different types of MnO$_2$ on the removal efficiencies of PCBs, experiments were carried out with the addition of 0.2 mL of water to 1.0 g of contaminated soil with the assistance of 0.1 g of α-MnO$_2$, β-MnO$_2$ and δ-MnO$_2$, respectively, for 45 min of MW irradiation. The results showed that δ-MnO$_2$ was more effective in degrading PCBs, followed by α-MnO$_2$ and β-MnO$_2$ (Figure 5). This result was in accordance with the reported oxidation capacity of these three types of MnO$_2$ [36], which followed an order of δ-MnO$_2$ (devoid of Mn$^3+$) > α-MnO$_2$ > β-MnO$_2$. On the other hand, the variety of the crystalloid state, the purity and the morphology of the three types of MnO$_2$ played important roles in the differences of their microwave adsorption capacities as reported by Duan et al. [18]. A flaky or strip-shaped structure had weaker microwave adsorption capacity than a spherical particulate because the former could form more dipole moments, which caused it to have more scattering cross-sections when subjected to electromagnetic radiation [18]. δ-MnO$_2$ was composed of granular and rod-shaped microparticles (Figure S2a, supplementary information), and the microwave absorption of δ-MnO$_2$ was high because δ-MnO$_2$ summed the attenuations of the different phases. The purity and crystallinity of α-MnO$_2$ and β-MnO$_2$, composed of nanorods and nanowires (Figure S2b and S2c, supplementary information), were greatly improved by contrast with δ-MnO$_2$, suggesting that the MW attenuation of α-MnO$_2$ and β-MnO$_2$ weakened accordingly.

3.7. Effect of acidic condition

Previous studies showed that acidic conditions could considerably affect the degradation of organic pollutants in soil by MW-irradiated MnO$_2$ [5,22]. Therefore, 0.2 mL of four concentrations (0, 1.0, 2.0 and 4.0 mol/L) of H$_2$SO$_4$...
solutions was added to investigate the effect of acidity on the removal of PCBs from actual polluted soil by MW-irradiated δ-MnO₂. The results are shown in Figure 6. The removal efficiencies of DiCB, TriCB, TetraCB and PentaCB increased from 95.9%, 82.5%, 52.0%, and 71.6% in the absence of H₂SO₄ to 100%, 87.9%, 64.5% and 72.8% in the presence of 1.0 mol/L H₂SO₄, respectively, indicating that low acidity could slightly promote the removal of low chlorinated biphenyls. However, the removal of 1.0 mol/L H₂SO₄ reduced the removal of high chlorinated biphenyls, such as HexaCB, HeptaCB and OctaCB. When the concentration of added H₂SO₄ solution was higher than 1.0 mol/L, the removal efficiencies of all selected PCBs slightly decreased with an increase in the concentration of added H₂SO₄ solution (Figure 6). The result that addition of acid solution decreased the removal of PCBs by MnO₂ was not in agreement with previous studies [5,22], but the destruction efficiencies of PCBs by iron nano-particles were also found to decrease with increasing acidity of the reaction system [34]. On the one hand, the addition of H⁺ enhanced the oxidation capacity of MnO₂, because H⁺ ions were required for reduction of MnO₂ to generate Mn²⁺ ions [37]. On the other hand, acidification of soil would alter the composition of clay mineral and humic compounds in the soil [38–40], thereby affecting the adsorption force of PCBs in soil. Therefore, when low concentrations of sulphuric acid solution were added to the soil–MnO₂ mixture, the oxidation capacity of MnO₂ increased, which resulted in the increased removal of low chlorinated biphenyls; however, the decrease in the removal efficiencies of high chlorinated biphenyls, such as HexaCB, HeptaCB and OctaCB, might be attributed to the greater difficulties in desorption from soil because of their higher hydrophobicity and stronger affinities for soil. In the same way, addition of high concentrations of sulphuric acid solution in soil might seriously change the composition and physical structure of the raw soil, which might result in the reduction of the transferable amount of PCBs from soil to MnO₂ surfaces and accordingly decrease the removal efficiencies of PCBs.

4. Conclusions
Compared to MW irradiation in the absence of both water and MnO₂, the removal efficiencies of PCBs from actual heavily PCB-contaminated soil were considerably raised by MW irradiation for 45 min with the assistance of water and MnO₂. The removal efficiencies of PCBs from contaminated soil were also found to considerably increase, although in a nonlinear fashion, as the MW irradiation time increased, and as the initial amounts of water and MnO₂ were increased. The generation of Mn²⁺ ions from δ-MnO₂ was increased with increasing removal of PCBs, indicating that δ-MnO₂ oxidized PCBs leading to its reduction to Mn²⁺ ions. Addition of different types of MnO₂ to PCB-contaminated soil caused a considerable difference in the removal efficiencies of PCBs, following the order of δ-MnO₂ > α-MnO₂ > β-MnO₂. This result was primarily attributed to the different oxidation capacities and electromagnetic characteristics of different types of MnO₂. Addition of acid would enhance the oxidation capacity of MnO₂ and disturb the transfer of PCBs from soil to the surface of MnO₂. Low concentration of H₂SO₄ was favourable for the removal of DiCB, TriCB, TetraCB and PentaCB from the soil, but high concentrations of H₂SO₄ were disadvantageous to the removal of all the PCBs. Great reductions in treatment time and pronounced removal efficiencies of PCBs, especially for low chlorinated biphenyls, were accomplished in this study, indicating that MW irradiation with the assistance of MnO₂ is an efficient and promising treatment technology for the remediation of heavily PCB-contaminated soil.

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