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Desorption, partitioning, and dechlorination characteristics of PCBs in sediments in interaction with reactive activated carbon

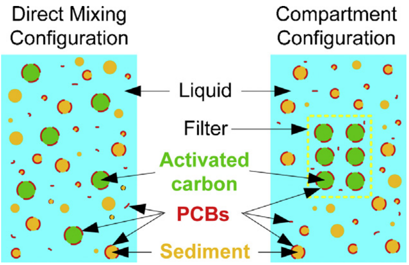
Hyeok Choi[a,b,*], Wasiu Lawal[b], Souhail R. Al-Abed[c]

[a] *Department of Civil Engineering, The University of Texas at Arlington, 416 Yates Street, Arlington, TX 76019-0308, USA*
[b] *Environmental and Earth Sciences Program, The University of Texas at Arlington, 500 Yates Street, Arlington, TX 76019-0049, USA*
[c] *National Risk Management Research Laboratory, U.S. Environmental Protection Agency, 26 W. Martin Luther King Dr., Cincinnati, OH 45268, USA*

HIGHLIGHTS

- Problematic aged real PCBs-contaminated sediment (WHS) was examined.
- Performance of reactive activated carbon (RAC) impregnated with Pd–ZVI was tested.
- Fate and transport of PCBs bound to WHS in the presence of RAC was fully traced.
- Direct mixing configuration was compared with compartment configuration.
- Results reflected real world complexities associated with slow desorption of PCBs.

GRAPHICAL ABSTRACT



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ABSTRACT

Sediment (WHS) in Waukegan Harbor, Illinois, heavily contaminated and aged with polychlorinated biphenyls (PCBs), was treated with reactive activated carbon (RAC) impregnated with palladized iron nanoparticles. Lab test proceeded in a direct mixing configuration of RAC and WHS. A compartment configuration, where RAC was physically separated from WHS, was also designed to trace the sequential transport and fate of PCBs, including desorption, adsorption, dechlorination, and re-partitioning. PCBs, once desorbed from WHS, were immediately sequestrated to RAC and subject to dechlorination. Direct mixing of WHS with RAC was one-order of magnitude more effective for dechlorination than compartment configuration. Compared to their desorption-followed by-adsorption route, direct physical contact of RAC with PCBs bound to WHS exhibited negligible contribution to the availability of PCBs for dechlorination reaction. Addition of RAC even in compartment configuration facilitated PCBs desorption from WHS. However, slow desorption of PCBs limited overall performance, resulting in a five-order of magnitude lower dechlorination yield when compared with treatment of purely aqueous PCBs. The low dechlorination yield reflected real world complexities in treating 3.19% organic carbon-containing WHS aged with PCBs for 40 years. These observations were further supported when compared with results on clean Cesar Creek sediment spiked with 2-chlorinated biphenyls.

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[*] Corresponding author at: Department of Civil Engineering, The University of Texas at Arlington, 416 Yates Street, Arlington, TX 76019-0308, USA. Tel.: +1 817 272 5116; fax: +1 817 272 2630.
E-mail address: hchoi@uta.edu (H. Choi).

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1. Introduction

Aqueous sediment contaminated with chlorinated organic compounds showing hydrophobic nature, such as polychlorinated biphenyls (PCBs) is a huge concern worldwide [1,2]. The United States (U.S.) Environmental Protection Agency (EPA) reported in 1998 that approximately 10% of the sediment in the U.S. poses potential environmental risk to fish, wildlife, and eventually humans [3]. Particular interest has been given to sediment in Waukegan Harbor (WHS), Waukegan, Illinois. The U.S. EPA investigations in 1976 revealed high levels of PCBs at the site [4]. PCBs above the U.S. Food and Drug Administration action levels of 2.0 mg/L were also found in resident fish species [5]. A dredging and disposal method could be an option for the remediation of WHS [6]. However, dredging at Waukegan Harbor is complicated, since PCBs contamination of inner harbor sediment and clean sediment moving along the lakeshore has raised some arguable dredging and disposal issues [4]. Along with its high cost, the principle of the method is just to relocate a contaminated site to elsewhere.

In situ capping with a physical barrier of clean sand has been proposed to isolate contaminated sites from the surrounding environment [6]. Strong adsorption ability of activated carbon (AC), when directly mixed with contaminated sediment or applied as a barrier (or cap), significantly reduces PCBs level in the aqueous phase and thus, their bioavailability [7,8]. Many studies reported the effectiveness of AC amendment to sequester hydrophobic organic contaminants in sediments, such as PCBs and also proposed PCB mass transfer modeling to predict the in situ treatment performance of AC [9–16]. In particular, 2 years of column experiments were conducted to simulate field conditions and revealed the fate and transport of PCBs over time [9,10]. Most of the studies pointed out the significance and implication of mass transfer limitation of PCBs in treating an actual sediment matrix. The AC-amended approaches do not chemically decompose PCBs, but only physically sequester them.

Meanwhile, effective electrochemical dechlorination of toxic PCBs to relatively biodegradable biphenyl (BP) has been reported using reactive metal particles (e.g., Fe and Mg) [17,18]. Most of the studies have treated aqueous phase PCBs simply to investigate mechanistic aspects of the dechlorination reaction (e.g., kinetics, intermediates, and treatability). However, PCBs in sediments are much less available for the reaction at metal surface, since PCBs are hard to desorb into water once they are adsorbed to sediment matrix. This is primarily because PCBs exhibit high affinity for organic substances in sediment and extremely low water solubility [19]. A few studies have treated spiked sediment with PCBs, since the spiked PCBs are much easier to desorb, compared to PCBs naturally aged with sediment for a long time [17,20]. Typical treatment protocol for PCBs-contaminated sediment proceeds basically in two consecutive steps: (i) facilitated desorption of PCBs to the aqueous phase containing co-solvents or surface modifiers and (ii) treatment of the desorbed PCBs by using available chemical techniques [21].

Most probably, because of real world complexities associated with PCBs desorption, it is difficult to find in literature that a reactive metal system was tested to treat actual sediment, where the fate and transport of PCBs in the remediation system would be interesting. Detailed mechanistic aspects of the underlying behavior, such as desorption of PCBs, their adsorption and subsequent dechlorination onto metal particles, and their ensuing partitioning, were neither conceptually considered nor experimentally elucidated. Tracing the detailed fate and transport of PCBs would be a key to successful understanding on the availability route of PCBs for the dechlorination reaction.

In this study, we, for the first time, demonstrated the treatment of PCBs-contaminated WHS (one of the most highly contaminated sediments in the U.S.) by using reactive activated carbon (RAC) impregnated with iron/palladium (Fe/Pd) bimetallic nanoparticles. As a new remediation tool, the RAC has been tested to elucidate the unique adsorption-mediated dechlorination strategy towards PCBs exclusively in the aqueous phase so far [22–26]. The objective of this study was to investigate the step reactions occurring during the treatment of a real sediment with RAC. A systematic lab-scale test was designed in manner of a direct mixing configuration or a compartment configuration to answer: (i) how PCBs desorb from WHS, (ii) how they transport and adsorb to RAC, (iii) how they dechlorinate onto RAC, and (iv) how they and reaction intermediates eventually partition to water, sediment solids, and RAC. Detailed discussion on the cost of the technology was out of the scope of this present study.

2. Experimental

2.1. RAC synthesis and WHS characterization

The detailed synthesis procedure of RAC containing 14.4% Fe and 0.7% Pd was reported previously [22]. Briefly, lignite-based mesoporous granular activated carbon (GAC) in grain size of 2–3 mm (density of 0.38 g/cm^3) after sieving was used as a base material (HD3000, Norit Americas Inc.). The mesoporous structure of GAC especially in the range of 7–40 nm was well occupied by the metal particles. The raw GAC with BET surface area of 574 m^2/g and pore volume of 0.639 cm^3/g was transformed to RAC with BET surface area of 358 m^2/g and pore volume of 0.352 cm^3/g [22]. Around 57% of Fe was in zerovalent state.

WHS was taken on September, 2007 from the inner harbor close to the source of PCBs. The aqueous sample was dried at 105 °C in an oven for 1 day and thus, solid sample was used as stock for further remediation experiments upon addition of water (this setup gives more flexibility in simulating various scenarios with different mixing ratios of sediment, AC, and water). The properties of WHS were characterized, including PCBs concentration (HP 6890 gas chromatograph/HP 5973 mass spectrometer), surface area (Micromeritics Tristar 3000), and organic carbon content (Shimadzu TOC analyzer with SSM-5000A solid module). The organic carbon was categorized into amorphous organic carbon and soot organic carbon [27]. After mixing 1.8 g of WHS with 22 mL of water for 1 day, supernatant was filtered using 0.45 μm GMF (Whatman). The pH (Thermo, Orion 370), conductivity (Thermo, Orion 5star), and dissolved organic carbon (TOC analyzer) of the supernatant were measured.

2.2. Sacrificial batch test in direct mixing and compartment configurations

Synthesis, storage, and handling of RAC were performed in an anaerobic glovebox under oxygen less than 0.05 mg/L and hydrogen 3.5%. Sediment experiments were based on sacrificial batches in anaerobic condition. If technically possible, most of the experimental procedures below from sample mixing, reaction over time to sample analysis were done in the anaerobic glovebox or under anaerobic condition within capped bottles. To investigate desorption of PCBs from WHS in the absence of AC materials, 1.8 g of WHS was mixed with 22 mL of water (control). Two additional sets of batch reactors were built with pristine GAC and GAC impregnated with Fe/Pd (i.e., RAC), where 0.6 g of the AC materials were directly mixed with WHS (direct mixing) under the same condition as control, as shown in Fig. 1(a).

The direct mixing configuration makes it difficult to separate AC materials and WHS solids. The separation is essential for understanding the partitioning behavior of PCBs between the two