Supporting Information

Effects of Ageing and Oxidation of Palladized Iron Embedded in Activated Carbon

on the Dechlorination of 2-Chlorobiphenyl

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Contents (7 pages including this cover)

Supplementary Description on Some Experimental Sections

Reproducibility of Experiment. Due to the characteristic of sacrificial batch set up for solid phase PCBs extraction, triplicates were run only in limited cases, if statistically essential. It is a little bit hard to triplicate due to too many sample production (extraction is limited). Especially, we intended to minimize the amount of samples since dechlorination capacity and dechlorination longevity tests needed too much amount of 2-ClBP (perhaps more importantly disposal issue of environmentally hazardous waste) and too long experimental period. Triplicated result on the oxygen effect in Figure 6, which was simple and did not require over-consumption of materials, implies the reproducibility of such an experiment. We believe that the experiment set up is enough to provide scientifically reliable information on dechlorination capacity and longevity.

Dechlorination Capacity Test (High Concentration of 2-ClBP and Use of Co-solvent). We used high concentration of 2-ClBP, which is around 5–6 orders of magnitude higher than its typical concentration found in the aqueous phase. This specific test is not directly related to its application to contaminated sites but to the fundamental and scientific aspects. With respect to the properties of RAC containing a certain amount of Fe, we wanted to investigate "how effective the Fe in RAC is to dechlorinate PCBs" and "how much of PCBs can be dechlorinated per unit mass of RAC". In order to achieve the purpose, we needed to make the reaction condition PCBs-rich. Based on our calculation, we needed to contact 2-ClBP with RAC in a mass ratio of at least 0.5. For example, in order to avoid use of any co-solvents, 1 g of RAC should be mixed with 100 L of 5 mg/L 2-ClBP solution in water. In this case, it is difficult to achieve intimate contact between the RAC and PCB while maintaining the structural integrity of RAC.

Perhaps more importantly, this route would also generate large amounts of environmentally hazardous waste that is extremely difficult and expensive to dispose off. Instead, we resorted to using methanol as a co-solvent to increase PCBs solubility. Here, 0.1 g of RAC (minimum amount for solid extraction) was added to 50 mL of 1057 mg/L 2-ClBP dissolved in methanol/water.

Organic solvents such as acetone, ethanol, and methanol to increase PCBs solubility are known to lower the polarity of water and thus reduce the readiness of water for electrolysis on the Fe/Pd systems. In addition, organic solvents increase the affinity of PCBs for the liquid phase. Some solvents compete with PCBs for reduction on Fe/Pd. These three effects definitely decrease the PCBs reaction kinetics but eventually do not significantly influence the overall dechlorination capacity of RAC for long term run in the presence of excessive amount of water for electrolysis on relatively small amount of Fe/Pd. Moreover, we chose methanol which is already reduced and thus does not consume the reactivity of RAC.

Automated Soxhlet. In order to investigate speciation of carbon in the AC phase, it is critical to extract 2-ClBP and BP as much as possible. Among extraction methods we have tried, the automated Soxhlet showed reasonably high extraction efficiency. The method uses a commercially available three-stage extraction system (Soxtec System HT, Tecator). Sample (0.1–1 g)-loaded extraction thimble (Munktell) was immersed into 20 mL of 50:50 acetone:hexane at 120 °C and ambient pressure for 2 h. The thimble was rinse-extracted, and then the solvent was evaporated. The extract was concentrated and exchanged into pure hexane prior to final measurement using the GC/MS. Extracts were analyzed in triplicates.
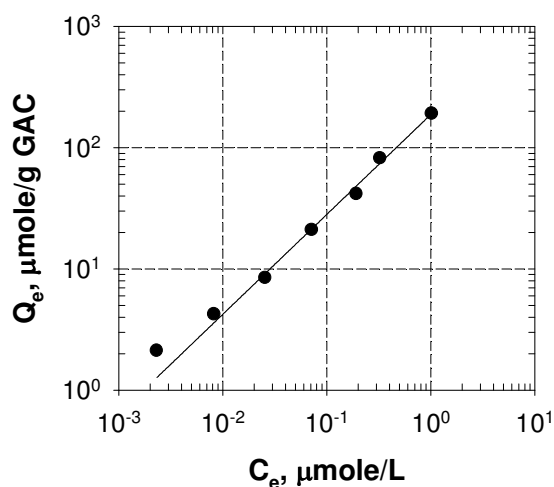
FIGURE S1. 2-ClBP adsorption isotherm to GAC. Due to the dechlorination of 2-ClBP adsorbed to RAC to BP, its adsorption isotherm to RAC is technically hard to define. There was no adsorption preference of the activated carbon between 2-ClBP and BP (reference 9 in the text). PCBs adsorption capacity of RAC might be slightly lower than that of GAC, considering the slightly lower surface area of RAC (358 m^2/g) than GAC (574 m^2/g) (reference 8 in the text). The line with $r^2 = 0.996$ is a fitting curve for the Freundlich model: $Q_e = K_F \times C_e^{1/n}$, where Q_e is 2-ClBP adsorbed to GAC (μmole/g), C_e is 2-ClBP remaining in liquid (μmole/L), K_F is the Freundlich sorption constant ((μmole/kg)/(μmole/L)$^{1/n}$), and $1/n$ is the Freundlich exponent at equilibrium. Note that 2-ClBP adsorption isotherm for RAC is hard to define due to the dechlorination of 2-ClBP to BP. The experiment was based on a batch test, involving adsorption equilibrium of 2-ClBP between the aqueous and GAC solid phases. A calculated amount of GAC followed by 200 mL of 2.0 mg/L 2-ClBP solution was added in a 250 ml borosilicate glass bottle with Teflon-lined caps (Fisher), making GAC/2-ClBP ratio of 5–500. The bottles were agitated in a gyrotory shaker (New Brunswick Scientific) at 150 rpm under dark condition at 20 ºC for 28 d.
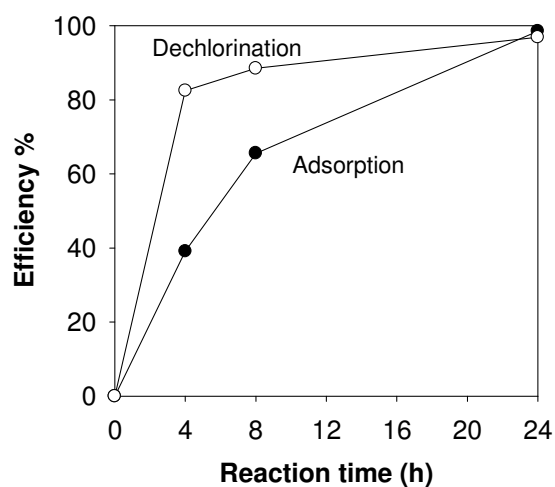
FIGURE S2. 2-ClBP adsorption and dechlorination kinetics on fresh RAC. Dechlorination efficiency in terms of solid phase dechlorination (i.e., BP formation from 2-ClBP adsorbed to RAC) corresponds to the reactivity of RAC. In order to compare the adsorption and dechlorination efficiencies of fresh RAC with those of aged RAC, 4 h was selected as a reasonable time frame (showing 39.1% adsorption and 82.5% solid phase dechlorination here).
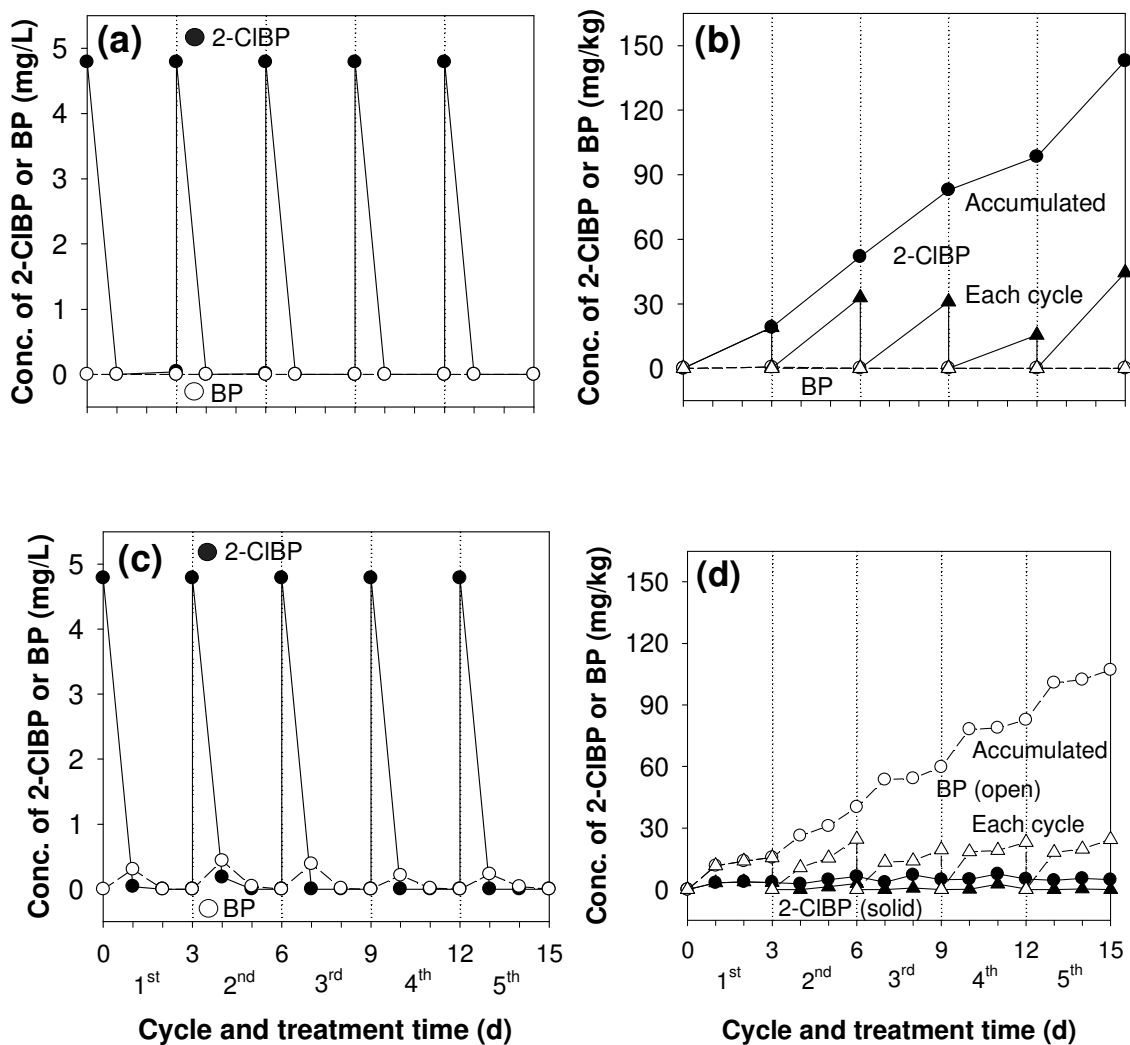
FIGURE S3. Evolution of 2-ClBP and BP concentrations in the liquid and solid phases during short term treatment of spiked 2-ClBP using GAC and RAC, where reacted 2-ClBP solution was replaced with new one in each cycle of 3 days: (a) 2-ClBP and BP in the liquid phase for GAC system, (b) 2-ClBP and BP observed in the solid phase for GAC system, (c) 2-ClBP and BP in the liquid phase for RAC system, and (d) 2-ClBP and BP observed in the solid phase for RAC system. The observed concentrations of 2-ClBP and BP in the AC solid phase are different from their actual concentration due to incomplete extraction of 2-ClBP and BP from the AC phase.
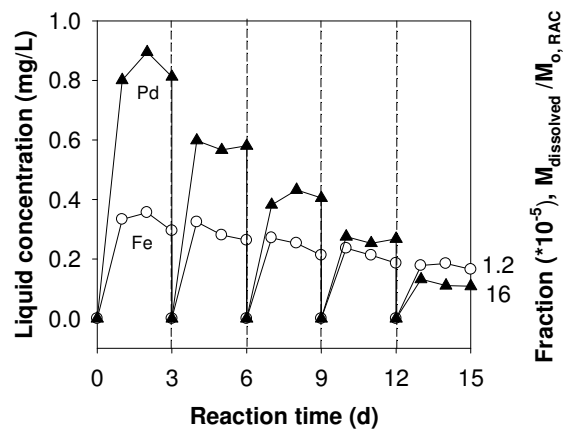
FIGURE S4. Fe and Pd leaching properties of RAC during 5 cycles 2-ClBP treatment shown in Figure 2.