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Adsorption and Simultaneous Dechlorination of PCBs on GAC/Fe/Pd: Mechanistic Aspects and Reactive Capping Barrier Concept

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There are many concerns and challenges in current remediation strategies for sediments contaminated with polychlorinated biphenyls (PCBs). Our efforts have been geared toward the development of granular activated carbon (GAC) impregnated with reactive iron/palladium (Fe/Pd) bimetallic nanoparticles (reactive activated carbon (RAC)). In this study, we elucidate the mechanistic aspects of the hybrid RAC system dechlorinating 2-chlorobiphenyl (2-ClBP) in the aqueous phase. The following reactions occurred in parallel or consecutively: (i) 2-ClBP is promptly and completely sequestrated to RAC phase, (ii) the adsorbed 2-ClBP is almost simultaneously dechlorinated by Fe/Pd particles to form a reaction product biphenyl (BP), and (iii) the BP formed is instantly and strongly adsorbed to RAC. The 2-ClBP adsorption and dechlorination rate constants were estimated through simple first-order reaction kinetic models with an assumption for unextractable portion of carbon in RAC. The extent of 2-ClBP accumulation and BP formation in RAC phase could be well explained by the kinetic model and adsorption was found to be the rate limiting step for overall reaction. On the basis of our observations, a new strategy and concept of "reactive" cap/barrier composed of RAC was proposed as a new environmental risk management option for PCBs-contaminated sites.

Introduction

Remediationof sediments contaminated with hydrophobic organic compounds, such as polychlorinated biphenyls (PCBs), remains a scientific and technical challenge. The high stability, low aqueous solubility, and high organic affinity of PCBs make them difficult to treat (*1*). Many physical, chemical, and biological remediation strategies have been proposed, including dredging, landfilling, incineration, biodecomposition, in situ capping, and electrochemical degradation (*1*−*4*). Among them, the use of reactive metals such as Fe and Mg in zerovalent state has been documented to work efficiently for the reductive dechlorination of PCBs and other chlorinated compounds (*3, 5*−*8*). The metallic system has been further advanced for enhanced reactivity through deposition of a discontinuous layer of noble metals on the substrate metal surface and manipulation of its properties in the nanoscale regime.

Because of its high reactivity, the nanoscale bimetallic system seems promising for treatment of aqueous PCBs in groundwater or equivalent because the dechlorination reaction occurs in water−metal interface. However, PCBs exhibit extremely high affinity for organic substances in sediment and low solubility in water (at most, 4−5 mg/L) (*9, 10*). PCBs adsorbed to sediment matrix are hard to desorb to liquid phase for their availability for dechlorination with the metallic particles (*10*−*13*). In addition, the fast dechlorination reaction by the metallic system with noncatalytic and consumable reactivity should be controlled to respond to the long-term slow release of PCBs in sediment to aqueous phase. Injection and dispersion of colloidal metal particles could be a critical hurdle for their in situ field applications (*11, 12*).

Meanwhile, in situ capping, employing a physical barrier of clean soil (e.g., sand layer) to isolate the contaminated sites from the surrounding environment, has been proposed to be an effective treatment strategy for PCBs-contaminated sediments (*2, 14*−*17*). The effectiveness of a cap is greatly improved by adding an activated carbon (AC) layer (*2, 15*) or by mixing AC directly with contaminated sediment (*16, 17*). In addition to the reduction of PCB concentration in aqueous phase, this decreases PCB uptake by living creatures in the environment such as earthworms and clams (*16, 18*). However, the high adsorption capacity and capillary effect of AC might facilitate desorption of PCBs in a stable sediment matrix to liquid phase that flows to the AC capping layer covered by a layer of clean top soil. The AC approach does not degrade PCBs; it only physically sequesters them. That might not be an ultimate solution because slight changes in the capping environment can cause the erosion of the capping layer and resuspension of the sequestered PCBs at high concentration.

To overcome the limitations of the current remediation strategies mentioned above, we have recently synthesized granular AC impregnated with Fe/Pd bimetallic nanoparticles (GAC/Fe/Pd or reactive AC (RAC)), particularly focusing on its synthesis route, including in situ incorporation of Fe particles in the GAC mesopores, modification of Fe surface with noble Pd, and nanoscaling of Fe and Pd particles (*19*). The RAC is a smart composite for dechlorination of PCBs because RAC with high adsorption capacity actively attracts hydrophobic PCBs in sediment matrix toward itself, unlike neat Fe/Pd which passively waits for contact with PCBs. The RAC system is expected to be highly complex even for liquid phase treatment because it comprises three materials (AC, Fe, Pd), at least two chemicals (2-ClBP, BP), and two phases (liquid, AC solid), and several reactions occur in parallel or consecutively. Carbon mass balance required for investigating the configuration of overall reaction in the RAC system is hard to set up because of incomplete extraction of PCBs and reaction products from the highly adsorptive GAC phase. In general, little has been elucidated on its mechanistic aspects.

In this study on the RAC system, our objective is to investigate mechanistic aspects of the adsorption and dechlorination of a PCB congener and partitioning of a reaction product biphenyl (BP) in contrast with neat GAC through sacrificial batch experiments with aqueous 2-chlorobiphenyl (2-ClBP) as a model PCB in the absence of other organic materials and ionic species. We also demonstrate the concept of a "reactive" capping barrier composed of the RAC for the remediation of PCBs-contaminated groundwater

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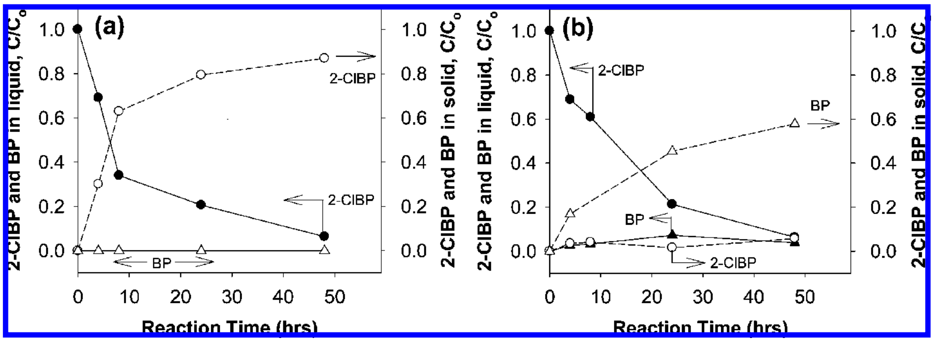


FIGURE 1. Evolution of adsorption of 2-ClBP to AC phase, transformation of the adsorbed 2-ClBP to BP, and partitioning of the formed BP between liquid and AC phases over time in (a) GAC and (b) RAC at the lowest loading of 5 g/L. The concentrations of 2-ClBP and BP were expressed in terms of mass fraction in overall system (i.e., C_0 is the initial concentration of 2-ClBP (4.08 mg/L) and the total amount of 2-ClBP and BP in liquid and AC phases should be equal to C_0). All the concentrations are observed values and expressed in terms of mass fraction. The concentrations of 2-ClBP and BP in liquid phase are their actual concentration while those in solid phase above are different from (lower than) their actual concentrations due to incomplete extraction of 2-ClBP and BP from AC.

and sediment and briefly discuss its general concerns to be addressed in future.

Experimental Section

Synthesis of RAC. The detailed synthesis procedure and route was demonstrated elsewhere (*19*). Briefly, iron was incorporated into mesoporous GAC (HD 3000, Norit Americas Inc.) in 2−3 mm size via an incipient wetness impregnation method. $Fe(NO_3)_3 \cdot 9H_2O$ (22.8 g, Fisher) was melted at 55−60 °C, mixed with 10 g of GAC, and then dried at 60−70 °C using an infrared ramp for 2 h. The GAC/$Fe(NO_3)_3$ composite was further calcined in a furnace (Paragon HT-22-D, Thermcraft) at 300 °C for 4 h to transform $Fe(NO_3)_3$ to Fe_2O_3 and sieved using a no. 20 sieve (U.S.A. Standard Testing Sieve) to remove unincorporated Fe_2O_3 particles. To reduce Fe_2O_3 to zerovalent Fe (ZVI, Fe^0), 1.6 g $NaBH_4$ (Fisher) dissolved in 20 mL water was added to 4 g GAC/Fe_2O_3 suspended in 50 mL of methanol/water (30/70 v/v) at pH 6.5. Then GAC/ZVI was recovered and washed with methanol to remove free ZVI and other impurities and then dried at room temperature. For Pd doping, the GAC/ZVI was mixed with 75 mg of palladium acetate ($Pd(CH_3CO_2)_2$, Sigma) dissolved in 20 mL methanol. Then GAC/ZVI/Pd (RAC) composite was recovered, washed, and dried again. All procedures for synthesis, storage, and handling of GAC/ZVI and RAC samples were performed in an anaerobic chamber (Forma Scientific), and samples at the end of each procedure were sieved with a no. 20 sieve to remove grains smaller than 0.85 mm.

Sacrificial Batch Reaction. Among PCB congeners, 2-ClBP was selected as a target PCB to adsorb and dechlorinate using GAC and RAC because it has the highest solubility in water up to 5.9 mg/L, it is the most persistent among mono PCB congeners for hydrodechlorination because of the ortho positional chlorine, and it transforms to a single dechlorination product BP, which allows us to focus on the evaluation of process kinetics. Simple sacrificial batch reactions were designed without real-world complexities to test adsorption and dechlorination reaction kinetics. In an anaerobic chamber, the desired amount of GAC or RAC was added into 40 mL glass vial (Fisher) containing 10 mL of around 4 mg/L 2-ClBP (99%, Accustandard) aqueous solution, and the vial was tightly capped with PTFE liner. The concentration of AC materials was at 5, 20, and 100 g/L, and control units without AC material were also set up. All experimental units were prepared at once with the 2-ClBP solution. The solution was agitated using a gyroshaker (Gyrotory Model G2, New Brunswick) at 90 rpm for 48 h (up to 10 d). At predetermined times of 0, 4, 8, 24, 48, 120, and 240 h, reactors were taken from the shaker and sacrificed for 2-ClBP and BP analysis.

Extraction and Analysis of PCBs. The liquid part was separated from solid AC. A liquid sample of 0.5 mL was withdrawn using a glass pipet and mixed with 1.5 mL organic extraction solvent hexane (Fisher) in 4 mL extraction glass vial (Fisher). After agitation of the extraction solution using a vortex (Model 231, Fisher) for 1 min, obvious phase separation between aqueous phase and hexane phase with 2-ClBP and BP was observed. Finally 0.5 mL of water-free supernatant organic phase was taken using glass pipet, spiked with 10 μL of the internal standard (200 mg/L D-8 naphthalene in dichloromethane), and analyzed in a gas chromatograph (GC, HP 6890)/mass spectrometer (MS, HP 5973) equipped with a Supelco SPB-5 30 m × 0.32 μm × 0.25 μm column (EPA Method 8082) at the method detection limit of 5 μg/L. To extract 2-ClBP and BP in AC phase and thus investigate carbon speciation, automated Soxhlet (EPA Method 3541) showing high extraction efficiency was adopted. The concentrations of 2-ClBP and BP were expressed in terms of mass fraction in overall system.

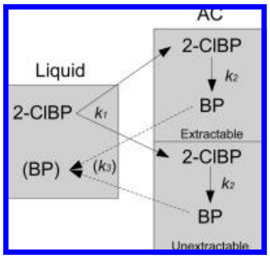
Results and Discussion

Adsorption and Dechlorination Behavior in GAC and RAC. The detailed properties of RAC were reported elsewhere (*19*). As shown in Figure S1 in the Supporting Information, an environmental scanning electron microscope image of RAC surface demonstrates that the mesoporous structure of GAC is clearly occupied by Fe/Pd bimetallic nanoparticles (around 14% and 0.68%, respectively).

Time evolution of 2-ClBP and BP concentrations in liquid and AC solid phases is demonstrated in Figure 1 (also note Figure S2 in Supporting Information). After 48 h of reaction, most of the 2-ClBP disappeared from the liquid phase while insignificant amount of BP remained in liquid phase, suggesting strong adsorption ability of AC for 2-ClBP and BP. For GAC, disappearance of 2-ClBP from liquid phase is solely attributed to its adsorption to GAC. As expected from no dechlorination reaction, accumulation of only 2-ClBP was observed in GAC solid phase. However, the amount of 2-ClBP accumulated in the solid phase was lower than that initially in solution because of incomplete extraction of 2-ClBP and BP from GAC phase.

Meanwhile, the RAC system is more complicated because of the dechlorination of 2-ClBP. Disappearance of 2-ClBP from liquid phase is initially caused by its adsorption to the RAC phase as in GAC system. 2-ClBP adsorption patterns in RAC were similar to those in GAC. However, the adsorption kinetics for RAC with surface area of 358 m^2/g was slower than that for neat GAC with more adsorptive sites (574 m^2/g). Time evolution of 2-ClBP and BP concentrations in RAC

SCHEME 1. Partitioning of 2-ClBP Remaining and BP Formed during Adsorption and Simultaneous Dechlorination of 2-ClBP[a]



[a] k_1, k_2, and k_3 indicate reaction rate constants. Desorption of BP formed in RAC phase to liquid phase is thermodynamically unfavored.

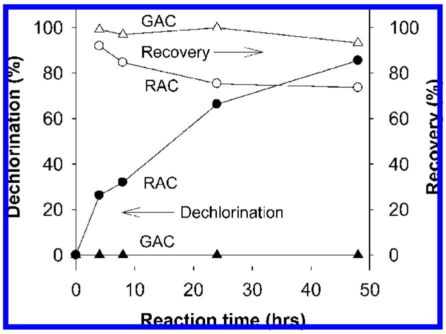


FIGURE 2. Apparent dechlorination efficiency and carbon recovery for GAC and RAC at the lowest loading of 5 g/L. Those were calculated on the basis of concentrations of BP and 2-ClBP observed in liquid and solid phases. Carbon recovery is slightly different from extraction efficiency, which is based on solid phase concentration, and thus, recovery is slightly higher than extraction efficiency.

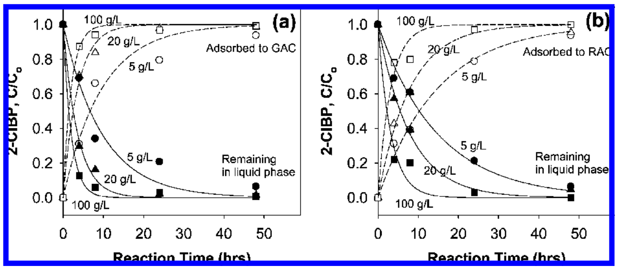


FIGURE 3. Kinetics of 2-ClBP adsorption to (a) GAC and (b) RAC at various loadings. This shows 2-ClBP remaining in liquid phase and corresponding 2-ClBP adsorbed to solid phase. Actual 2-ClBP concentration in GAC solid phase is identical to the 2-ClBP amount adsorbed to GAC because there is no dechlorination reaction, while that in RAC solid phase is different from (lower than) the 2-ClBP amount adsorbed because of transformation of adsorbed 2-ClBP to BP. The lines indicate the fitting curves for first order adsorption reaction demonstrated in eqs 1 and 2.

solid phase is intriguing. In case the dechlorination reaction is slow compared to adsorption and thus limits the overall reaction of the system, 2-ClBP can be expected to accumulate in RAC (as for GAC system with no dechlorination, which showed accumulation of 2-ClBP). However, because 2-ClBP was negligible, while BP was predominantly observed in the RAC solid phase, the dechlorination reaction here was fast enough to immediately treat the 2-ClBP once adsorbed. This implies that the first step of the overall reaction is adsorption of 2-ClBP onto RAC and the adsorption step is rate limiting in RAC system, even though slight accumulation of 2-ClBP in RAC solid phase was observed in the early stage of the reaction. Importantly, BP was partitioned to RAC phase, implying instant adsorption of BP when formed.

Mass Balance. Carbon mass balance in the RAC system is demonstrated in Scheme 1. 2-ClBP is partitioned to liquid and RAC phases, along with BP formed from the dechlorination of the 2-ClBP. Unfortunately, incomplete extraction of carbon species from the AC phase because of the high affinity of AC for hydrophobic 2-ClBP and BP always induces uncertainty of the ratio of 2-ClBP/BP in the unextractable portion (*9*). On the basis of the mass balance, however, we know the sum of 2-ClBP and BP. Since our preliminary adsorption and extraction experiments performed with individual 2-ClBP and BP showed no preferred affinity of the GAC between them (note Figure S3 in Supporting Information), we assume that the ratio of 2-ClBP to BP in the unextracted portion is the same as that observed from extracted portion.

Dechlorination Efficiency and Recovery. The apparent dechlorination efficiency of GAC and RAC at 5 g/L loading and 2-ClBP and BP recovery from the systems are shown in Figure 2. For GAC system with no dechlorination reaction, high recovery of 2-ClBP was achieved at 93−100% and was stable over time, regardless of the extent of GAC loading. Meanwhile, RAC even at 5 g/L loading achieved 86% dechlorination in 2 days, while RAC at 20 and 100 g/L loading achieved almost complete dechlorination within 1 day. Interestingly, recovery of 2-ClBP and BP (mostly BP) for RAC was much lower than that for GAC and kept decreasing down to 74% upon completion of the reaction. This trend was more prominent in case of high RAC loading showing higher dechlorination. The poor recovery implies that BP formed during 2-ClBP dechlorination reaction is hard to desorb most probably because of strong interactions between BP and Fe/Pd particles. This can partly explain why most of BP formed is present in RAC solid phase. However, we can not rule out that (i) the RAC reduces 2-ClBP to beyond BP such as phenylcyclohexane and bicyclohexane for which the GC/MS method had not been set up or that (ii) generated BP polymerizes on the RAC (not very likely) (*5*, *20*).

Adsorption Kinetics. The concentrations of 2-ClBP remaining in liquid phase and thus 2-ClBP adsorbed to solid phase over time are demonstrated in Figure 3. In case of GAC, BP concentration in all phases is negligible because there is no dechlorination reaction and thus the amount of 2-ClBP adsorbed to GAC is identical to the actual concentration of 2-ClBP in GAC phase. However, for RAC system, the actual concentration of 2-ClBP in solid phase is different from the amount of 2-ClBP adsorbed because of transformation of adsorbed 2-ClBP to BP. Considering the high adsorptive capacity of AC and initial low concentration of 2-ClBP, disappearance of 2-ClBP from liquid and corresponding adsorption of 2-ClBP to solid follow first-order reaction kinetics (*21*)

$$C_{\text{remaining 2-ClBP, liquid}}/C_{\text{o}} = e^{-k_1 \times t} \qquad (1)$$

$$C_{\text{adsorbed 2-ClBP, solid}}/C_{\text{o}} = 1 - e^{-k_1 \times t} \qquad (2)$$

where $C_{\text{remaining 2-ClBP, liquid}}$ is the concentration of 2-ClBP in liquid phase, C_{o} is initial concentration of 2-ClBP at 4.08 mg/L, k_1 (h^{-1}) is first-order rate constant for the disappearance of 2-ClBP from the liquid phase (or 2-ClBP adsorption to solid phase), $C_{\text{adsorbed 2-ClBP, solid}}$ is amount of 2-ClBP adsorbed to solid phase, and t (h) is time. The first-order kinetic models fitted well to the experimental data with regression coefficient R^2 of above 0.95 in most cases. The rate constants measured from the fitting curves are presented in Table 1. As the solid loading was increased from 5 to 20 to 100 g/L, the rate constant for RAC was increased from 0.067 to 0.125 to 0.311 h^{-1}, which is slightly lower than that of neat GAC at 0.103, 0.278, and 0.495 h^{-1}.

TABLE 1. 2-ClBP Adsorption and Dechlorination Reaction Kinetic Constants for GAC and RAC

AC material	loading (g/L)	adsorption		dechlorination[a]	
		k_1 (h^{-1})	R^2	k_2 (h^{-1})	R^2
GAC					
	5	0.103	0.951	0	
	20	0.278	0.993	0	
	100	0.495	0.996	0	
RAC					
	5	0.067	0.988	0.168	0.925
	20	0.125	0.874	0.211	0.825
	100	0.311	0.971	0.430	0.942

[a] The dechlorination rate constants were estimated assuming that the ratio of 2-ClBP to BP in the unextracted portion of RAC is the same as that observed from extracted portion in each RAC loading

Dechlorination Kinetics. The 2-ClBP adsorbed to RAC was confirmed to be simultaneously dechlorinated by Fe/Pd particles on RAC. As typically observed (*22*), disappearance of 2-ClBP in solid phase by its dechlorination and corresponding formation of BP in solid phase follow first-order reaction kinetics. Consequently, overall adsorption and dechlorination reaction in RAC solid phase could be expressed as

$$C_{\text{actual 2-ClBP, solid}}/C_o = (1 - e^{-k_1 \times t}) \times e^{-k_2 \times t} \tag{3}$$

$$t = 0,\ C_{\text{actual 2-ClBP, solid}} = 0 \text{ mg/L}$$

$$t = \infty,\ C_{\text{actual 2-ClBP, solid}} = 0 \text{ mg/L}$$

$$C_{\text{formed BP, solid}}/C_o = (1 - e^{-k_1 \times t}) \times (1 - e^{-k_2 \times t}) \tag{4}$$

$$t = 0,\ C_{\text{formed BP, solid}} = 0 \text{ mg/L}$$

$$t = \infty,\ C_{\text{formed BP, solid}} = C_o$$

where $C_{\text{actual 2-ClBP, solid}}$ is actual concentration of 2-ClBP in solid phase, k_2 (h^{-1}) is first-order rate constant for dechlorination of 2-ClBP in RAC phase (i.e., formation of BP in RAC phase), and $C_{\text{formed BP, solid}}$ is concentration of BP in solid phase. In the equations, it was assumed that RAC has enough capacity to eventually dechlorinate all 2-ClBP provided (confirmed for 10 d experiment). Unfortunately, k_2 is impossible to measure since the exact amounts of 2-ClBP remained and BP formed in solid phase are unknown, as discussed. Hence, for the estimation of k_2, the ratio of 2-ClBP and BP in unextracted solid phase was assumed to be the same as that observed from extracted portion.

The assumed 2-ClBP and BP concentrations in RAC phase and fitting curves for the estimation of dechlorination rate constant k_2 at the given 2-ClBP adsorption rate constant k_1 (demonstrated in Table 1) in each RAC loading are shown in Figure 4. The kinetic model for RAC system is generally in agreement with its reaction behavior observed, prompt adsorption and simultaneous dechlorination. Regardless of the magnitude of k_2, adsorption of 2-ClBP to RAC with high adsorption capacity keeps progressing until all 2-ClBP provided is adsorbed. As shown in Figure 4, if k_2 is small (e.g., 0.1 for 5 g/L loading and 0.3 for 100 g/L loading), 2-ClBP adsorbed to RAC is more or less accumulated in solid phase over time, waiting for the subsequent dechlorination reaction with Fe/Pd particles on GAC. As time goes on, amount of 2-ClBP adsorbed from liquid phase decreases while dechlorination of 2-ClBP adsorbed to RAC continues to occur, and eventually 2-ClBP completely disappears from solid phase and only BP is present. The extent of 2-ClBP accumulation and BP formation in the solid phase is dependent on both k_1 and k_2 summarized in Table 1. When RAC loading is increased from 5 to 20 to 100 g/L, k_2 increased from 0.168 to 0.211 to 0.430 h^{-1}. At a high RAC loading of 100 g/L compared to 5 g/L, slightly more accumulation of 2-ClBP in RAC phase was observed at the earlier stage of the reaction because of its overwhelmingly faster initial adsorption ability. On the basis of the k_1 and k_2 for RAC, the adsorption event was found to be a rate limiting step for overall reaction in the RAC system.

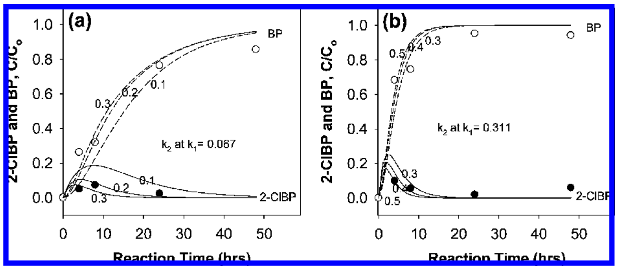


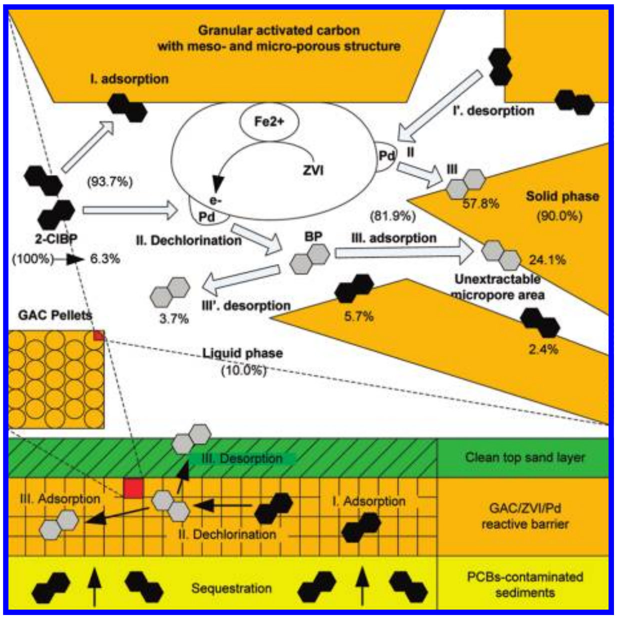
FIGURE 4. Estimation of first-order rate constant of 2-ClBP dechlorination (BP formation) reaction, k_2 for RAC at loading of (a) 5g/L and (b) 100 g/L. For the estimation, it was assumed that the ratio of 2-ClBP to BP in the unextracted portion of RAC is the same as that observed from extracted portion. The data points are assumed 2-ClBP and BP concentrations in RAC solid phase and lines are fitting curves to eqs 3 and 4 to estimate k_2 at the given adsorption reaction rate constant k_1. The total amount of 2-ClBP and BP in solid phase above is the same as the amount of 2-ClBP adsorbed to RAC demonstrated in Figure 3b.

In Figure 2, demonstrating the relatively low BP and 2-ClBP recovery in RAC system, we already implied that BP formed might be bound strongly to RAC matrix and thus harder to extract than 2-ClBP. This strongly suggests that carbon unextracted from RAC phase is mostly BP, rather than being present proportionally to the ratio of 2-ClBP to BP observed in the extracted portion. As a result, we might have underestimated the concentration of BP formed in solid phase, as observed in Figure 4 (i.e., lower BP concentration and higher 2-ClBP concentration than those from the fittings). In that case, true dechlorination efficiency of RAC might be slightly higher than the apparent dechlorination efficiency shown in Figure 2.

Reactive Cap/Barrier Concept and Ongoing Research Needs. The treatment demonstrated so far is for the best case scenario in the first stage of the technology development. The dechlorination kinetics and efficiency of RAC might be slow and depreciated, respectively, in real-world treatment of PCBs-contaminated water containing (i) natural organic matter and soot carbon materials, which strongly adsorb PCBs (*9, 10*), and (ii) ionic species, which compete with PCBs for electrons generated (*23*).

On the basis of the results so far, the concept of a "reactive" cap/barrier composed of RAC pellets contained between thin geo-textile membranes is proposed in Scheme 2 (*2, 15*). These caps can be installed horizontally at the bottom of estuaries and river banks to contain PCB-contaminated sediments. Alternatively, the RAC can be directly mixed with the PCB-contaminated matrix for more prompt sequestration of PCBs (*16, 17*), while the RAC barrier can also be installed vertically for flow-through treatment of PCBs-contaminated groundwater. The reactions in the barrier/cap are complex. As time goes on, most of PCBs might still remain in the stable sediment matrix, especially the organic fraction of the sediment. Upon their desorption to aqueous phase and movement to the surrounding environment, PCBs are promptly sequestrated in the RAC barrier. Some of the PCBs are strongly adsorbed and some are dechlorinated to form reaction intermediates and eventually BP, which are also rapidly and strongly adsorbed to RAC or diffused in

SCHEME 2. Conceptual Schematic of a "Reactive" Capping Barrier Composed of GAC Impregnated with Fe/Pd Bimetallic Particles (noted as RAC) for the Adsorption and Simultaneous Dechlorination of PCBs in Sediments[a]



[a] The mass balance of 2-ClBP (black bihexagonals) and BP (gray bihexagonals) in liquid and solid phases after 48 h of reaction with RAC at the lowest loading of 5 g/L is expressed in terms of mass fraction.

negligible amounts to bulk liquid phase. Possibly, PCBs remaining in aqueous phase and those adsorbed to solid phase are redistributed upon the reactions. Consequently, the engineered top sand layer is free from PCBs and reaction intermediates. A simple mass balance is expressed in Scheme 2. After 48 h of reaction with RAC at the lowest loading of 5 g/L, 2-ClBP and BP were partitioned at 6.3% and 3.7% in liquid phase and 8.1% ($5.7\%_{\text{extracted}} + 2.4\%_{\text{unextracted}}$) and 81.9% ($57.8\%_{\text{extracted}} + 24.1\%_{\text{unextracted}}$) in solid phase, respectively. This supports promising sequestration and dechlorination function of the RAC capping barrier as an effective option for environmental risk management of PCBs-contaminated sites.

Before its scale up and field applications, however, the high cost of RAC material because of the Pd doping, as well as the time-consuming procedures for RAC synthesis, needs to be reduced. In general, GAC determines PCBs adsorption capacity, ZVI is consumed upon production of electrons, and Pd as a catalyst rules the dechlorination kinetics. However, the three materials are closely related each other, and together they affect the overall adsorption and dechlorination reaction. Consequently, some critical issues such as Fe and Pd leaching (which are important for environmental aspects), adsorption, and dechlorination capacity and yield of RAC, and their aging and oxidation are currently being investigated along with initial demonstration of PCBs-contaminated sediment remediation using RAC.

Acknowledgments

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Supporting Information Available

ESEM image of RAC surface (Figure S1), 2-ClBP adsorption and dechlorination using 100 g/L of GAC and RAC (Figure S2), and comparative adsorption of individual 2-ClBP and BP to GAC (Figure S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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