



# Remediation of hexachlorobenzene contaminated soils by rhamnolipid enhanced soil washing coupled with activated carbon selective adsorption

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## ABSTRACT

The present study investigates the selective adsorption of hexachlorobenzene (HCB) from rhamnolipid solution by a powdered activated carbon (PAC). A combined soil washing-PAC adsorption technique is further evaluated on the removal of HCB from two soils, a spiked kaolin and a contaminated real soil. PAC at a dosage of 10 g L<sup>-1</sup> could achieve a HCB removal of 80–99% with initial HCB and rhamnolipid concentrations of 1 mg L<sup>-1</sup> and 3.3–25 g L<sup>-1</sup>, respectively. The corresponding adsorptive loss of rhamnolipid was 8–19%. Successive soil washing-PAC adsorption tests (new soil sample was subjected to washing for each cycle) showed encouraging leaching and adsorption performances for HCB. When 25 g L<sup>-1</sup> rhamnolipid solution was applied, HCB leaching from soils was 55–71% for three cycles of washing, and HCB removal by PAC was nearly 90%. An overall 86% and 88% removal of HCB were obtained for kaolin and real soil, respectively, by using the combined process to wash one soil sample for twice. Our investigation suggests that coupling AC adsorption with biosurfactant-enhanced soil washing is a promising alternative to remove hydrophobic organic compounds from soils.

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## 1. Introduction

Remediation of soils contaminated with hydrophobic organic compounds (HOCs) has aroused intensive attention of environmental scientists in the past decades. Surfactant-enhanced soil washing is proposed as an efficient clean-up technology especially for HOCs-contaminated soils [1–3]. Chemical surfactants, mostly anionic and nonionic, are proved capable of removing a variety of HOCs, such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyl and pesticides from soils [4–6]. Recently, increasing interests have been paid to the application of biosurfactants in soil washing, considering their superior environmental compatibility relative to the chemical surfactants [7–9]. For instance, rhamnolipids are widely studied as an enhancing agent to remediate soils with HOCs or heavy metals [8,10,11].

Rhamnolipids are mostly produced by *Pseudomonas aeruginosa*, which are composed of one or two rhamnose molecules as a hydrophilic portion, and up to three molecules of hydroxy fatty acids (C8–C14) as a hydrophobic portion. Abundant results have revealed that rhamnolipids can effectively mobilize or remove PAHs, oil, and PCP in soils [7,12]. More interestingly, it is sug-

gested that the residue of rhamnolipids in soils could promote the biodegradation of residual HOCs [13,14], which is also superior to the chemical surfactants.

However, whatever surfactants are used, post-treatment of their washing solutions is required to remove the contaminants, and moreover, to recover/reuse the surfactants. Unfortunately, up to now limited efforts have been devoted into the disposal of the washing solutions. Recently, some researchers reported that advanced oxidation processes (AOPs), such as photo-Fenton [15], photocatalytic [16,17] and electrochemical treatment [18] could effectively destruct the pollutants in surfactants solutions. Nevertheless, as AOPs are mostly associated with non-specific hydroxyl radical reactions, the presence of high concentrations of surfactants would inevitably impede the degradation of target contaminants. As a consequence, either a higher treating cost or a lower surfactants recovery would be expected. In this sense, the results of Ahn et al. [19] seem much more appealing, who found that granular activated carbon (GAC) could selectively adsorb phenanthrene from Triton X-100 solution. A high removal of contaminants (86.5%) and a high recovery of surfactants (93.6%) were obtained by using Darco 20–40 activated carbon (AC) at 1 g L<sup>-1</sup> [19,20]. Furthermore, the spent ACs could be further regenerated via either thermal or chemical methods, and reused for soil washing solution treatment. It was suggested that the adsorption process was simple, fast, and cost-efficient, therefore an applicable alternative to recover surfactants in soil washing technique [19].

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**Table 1**  
Selected physical–chemical properties associated with soils.

Property	Kaolin	Real soil
Particle size distribution <sup>a</sup> (%)		
1.0–0.25 mm	0.0	0.0
0.25–0.05 mm	3.7	1.8
0.05–0.005 mm	25.3	25.9
0.005–0.001 mm	19.6	32.6
<0.001 mm	51.4	39.7
Organic content <sup>b</sup> (%)	0.3	4.1
pH <sup>c</sup>	5.8	5.5
HCB concentration (mg kg <sup>-1</sup> )	11.3	20.8
USCS classification	Clay	Clay

<sup>a</sup> Hydrometer method by a TM-85 soil densimeter (Shanghai Tianle Electromagnetic Institute, China).

<sup>b</sup> Potassium dichromate digestion.

<sup>c</sup> Soil/water 1:1, with a pH meter (Hanna, pH-211).

In the present study we aimed to investigate the performance of AC in the selective adsorption of HOCs from biosurfactants solution, and the feasibility of remediating HOCs-contaminated soils by combining the AC adsorption process with biosurfactant-enhanced soil washing. Hexachlorobenzene (HCB) was chosen as the representative HOC, and rhamnolipid was selected as the typical biosurfactant. Two soils, a HCB-spiked kaolin and a real HCB-contaminated soil, were used. Our study was supposed to provide further information regarding the practical applicability of biosurfactants in soil washing.

## 2. Materials and methods

### 2.1. Chemicals and soils

HCB (99.0%) was obtained from Shanghai General Reagent Factory, China. Kaolin (chemical purity, Shanghai Qingpu Chemical Co. Ltd.) was spiked artificially with HCB [21] and aged for over one year before use. The real soil, also highly clayed, was taken from a site adjacent to a chemical plant in Wuhan, China. Selected physical–chemical properties associated with the two soils are listed in Table 1.

Commercial rhamnolipid powder was purchased from Urumchi Unite Biotech Co. Ltd., Sinkiang, China and partially purified for use (according to the manufacturer, the rhamnolipid was produced by *Pseudomonas aeruginosa* using soybean oil as a carbon resource. The culture supernatant was concentrated by adding 0.5% calcium chloride, dried under 60 °C then vacuum packed). The purification procedures for the rhamnolipid powder were as follows: about 100 g of the powder was blended with 500 mL of NaHCO<sub>3</sub> solution (0.05 M). The mixture was centrifuged at 12,000 rpm for 15 min, then the supernatant was extracted with ethyl acetate at 1:1 (v/v) for twice, and the combined organic phase was evaporated to obtain the raw rhamnolipid solid. The raw rhamnolipid was further purified for twice, then stored for use. A small portion of the obtained rhamnolipid was further purified according to procedures in literature [7] and characterized by LC–ESI–MS (Agilent 1100 LC/MSD trap) [22]. The rhamnose content was measured by sulfuric acid-phenol method similar to Zhang and Miller [23] using L-rhamnose as a standard. The critical micelle concentration (CMC) was determined by surface tension measurement using a surface tensionmat (Model JK99B, Shanghai Zhongchen) and the Du Nouy ring method [24].

Wood-based AC was purchased from Tianjin Tianda Purification Material Fine Chemical Plant, China. It was fractured and filtered through sieves of 14, 50, and 100 mesh sequentially, and the fractions of 14–50 mesh and <100 mesh were collected, designated as GAC and powdered AC (PAC) herein, respectively. Then the GAC and PAC were boiled in deionized water for 30 min, purged with deion-

ized water for several times, then dried under 105 °C over night and stored in a dryer for use. The BET specific surface areas measured by surface area apparatus (Micromeritics Tristar 3000) were 682 and 1297 m<sup>2</sup> g<sup>-1</sup>, and the pore volumes were 0.38 and 0.67 mL g<sup>-1</sup> for GAC and PAC, respectively.

### 2.2. HCB solubilization and enhanced desorption by rhamnolipid

The solubilization and desorption experiments were conducted in triple using batch equilibrium method as described previously [21]. In brief, excess solid HCB (for solubilization) or 0.5 g of HCB-spiked kaolin (for desorption) was mixed with 5 mL of rhamnolipid solution and agitated in a reciprocating shaker for 48 h (pH 7.0 ± 0.1). After centrifugation and filtration, the supernatant was extracted by hexane and analyzed for HCB by gas chromatography (GC). For desorption experiments, rhamnolipid concentration in filtrate was also measured by a tensionmat.

### 2.3. Adsorption of HCB from rhamnolipid solution by AC

All batch adsorption experiments were conducted in 100 mL flasks in duplicate. Firstly, to compare the efficiency of GAC and PAC on HCB removal from rhamnolipid solution, 0.05–0.2 g of GAC or PAC particles were mixed with 20 mL of solution containing 7.5 g L<sup>-1</sup> rhamnolipid and 1.0 mg L<sup>-1</sup> HCB (pH 7.0 ± 0.1). The mixture was agitated in a reciprocating shaker at 200 rpm and 30 ± 1 °C for 6 h (preliminary adsorption kinetic experiments indicated that when 10 g L<sup>-1</sup> PAC or GAC was used, HCB removal increased gradually within 0–6 h, then leveled off after 6 h). The mixture was then centrifuged under 12,000 rpm and the supernatant was filtered through a 0.45 μm acetate membrane, then subjected to HCB and rhamnolipid analysis. The effect of rhamnolipid concentration on the selectivity of PAC (GAC was not chosen given its insufficient HCB removal, see Section 3.3) was further investigated. The procedures were generally followed the adsorption experiments aforementioned, with the exception that the amount of PAC was kept as 10 g L<sup>-1</sup>, meanwhile a series of initial rhamnolipid concentrations (3.3–25 g L<sup>-1</sup>) were employed.

### 2.4. Soil remediation by soil washing coupled with AC adsorption

Successive soil washing–AC adsorption experiments were conducted firstly, which included three cycles of soil washing and two cycles of PAC selective adsorption treatments. Two soils, kaolin and real soil, were tested, and two rhamnolipid dosage, 12.5 and 25 g L<sup>-1</sup>, were employed. To begin with, 2.5 g of soils were mixed with 25 mL of rhamnolipid solution in a 100 mL flask (designated as Soil Washing Cycle 1, SW1), and 200 mg L<sup>-1</sup> sodium azide was contained to avoid any biodegradation process. After equilibrium and centrifugation, 20 mL of the resultant washing solution was mixed with 0.2 g of PAC, agitated for 6 h to remove HCB and regenerate the rhamnolipid solution (designated as AC adsorption Cycle 1, AC1). Then the regenerated rhamnolipid solution was used to start a new cycle of soil washing (designated as SW2) and AC adsorption (designated as AC2), and repeated again until the third cycle of soil washing (designated as SW3). The solution/soil ratio for soil washing was kept as 10 and the AC dosage for adsorption was kept as 10 g L<sup>-1</sup>. Both HCB and rhamnolipid analysis were performed for rhamnolipid solution at each stage of remediation (SW1–3, AC1–2). All other operations were the same as Sections 2.2 and 2.3.

The combined soil washing–AC adsorption process was further used to wash the same portion of soils repeatedly to achieve a desirable HCB removal. A total of 0.5 g of soils (kaolin or real soil) were firstly washed by 5 mL of rhamnolipid solution (25 g L<sup>-1</sup>) in glass tubes (designated as SW1). Ten parallel samples were prepared for each soil, and five were set as a group. The tubes were then cen-

**Table 2**  
Composition of present rhamnolipid mix identified by HPLC–ESI–MS.

No.	Composites	Pseudomolecular ion, <i>m/z</i>	Relative abundance, %
1	RhC <sub>8</sub>	305	1.0
2	RhC <sub>10</sub>	333	11.8
3	RhC <sub>12</sub>	361	0.7
4	RhC <sub>8</sub> C <sub>10</sub>	475	4.6
5	RhC <sub>10</sub> C <sub>10</sub>	503	21.6
6	RhC <sub>12:1</sub> C <sub>10</sub>	529	6.4
7	RhC <sub>10</sub> C <sub>12</sub>	531	7.5
8	Rh <sub>2</sub> C <sub>10</sub>	479	6.5
9	Rh <sub>2</sub> C <sub>8</sub> C <sub>8</sub>	593	0.4
10	Rh <sub>2</sub> C <sub>10</sub> C <sub>8</sub>	621	7.7
11	Rh <sub>2</sub> C <sub>10</sub> C <sub>10</sub>	649	20.9
12	Rh <sub>2</sub> C <sub>12:1</sub> C <sub>10</sub>	675	4.7
13	Rh <sub>2</sub> C <sub>12</sub> C <sub>10</sub>	677	6.3

trifuged at 4000 rpm for 20 min, and each group supernatant were decanted and combined. After filtration, 20 mL of the washing solution was subjected to the AC adsorption experiment (designated as AC1). Then 5 mL of the regenerated rhamnolipid solution was added to the tubes containing the precipitated soils (from SW1) to start the second cycle of washing (designated as SW2). All other operations were the same as the successive soil washing-AC adsorption experiments described above.

### 2.5. Chemical analysis

HCB in the hexane was determined on a Hewlett-Packard 6890 GC equipped with an electron capture detector and a ZB-5 capillary column (Phenomenex, USA). Detailed information for GC procedure was included in our previous study [21]. Aqueous rhamnolipid concentration was estimated by surface tension using a surface tensionmat employing the Du Nouy ring method [24]. The sample was diluted appropriately to ensure that the rhamnolipid concentration was below CMC. A calibration curve was constructed which related rhamnolipid concentration (mg L<sup>-1</sup>) to surface tension (dyn cm<sup>-1</sup>).

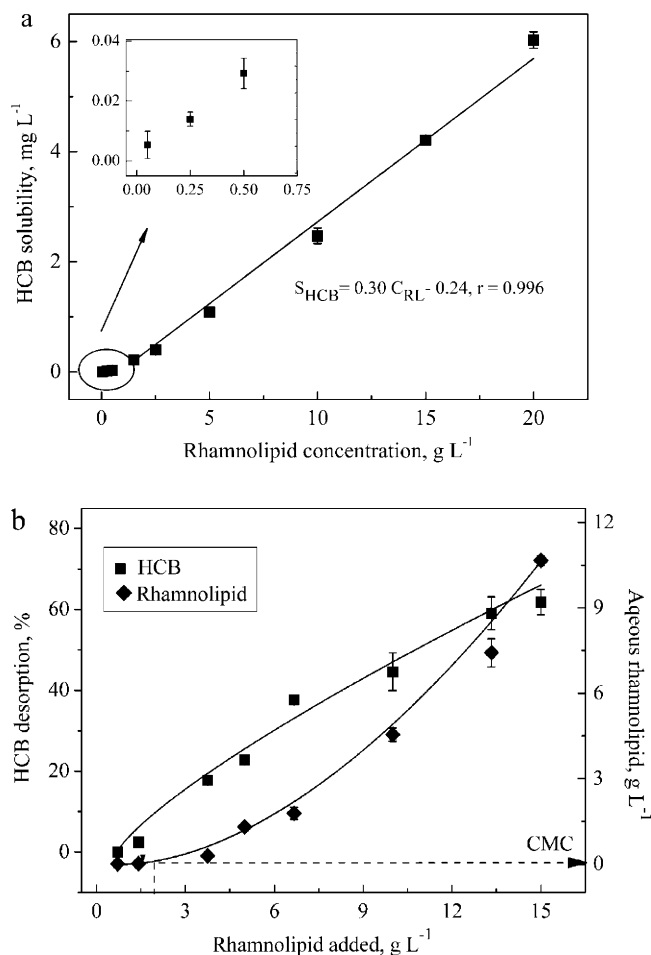
## 3. Results and discussion

### 3.1. Characterization of rhamnolipid

The composition of rhamnolipid identified by HPLC–ESI–MS is listed in Table 2. A total of 13 composites were detected, with 53.6% of monorhamnolipids and 46.4% of dirhamnolipids. Furthermore, RhC<sub>10</sub>C<sub>10</sub> accounted for the largest fraction of 21.6%, followed by Rh<sub>2</sub>C<sub>10</sub>C<sub>10</sub> of 20.9%. The fractions for RhC<sub>10</sub>, RhC<sub>10</sub>C<sub>8</sub> and Rh<sub>2</sub>C<sub>10</sub>C<sub>8</sub> were also considerable. The average relative molecular weight of the mix was estimated as 539.8 according to the composition information in Table 2. Correspondingly, the rhamnose content of the mix would be 44%. Based on the theoretical rhamnose content and the result measured by sulfuric acid-phenol method, purity of the rhamnolipid used for experiments was calculated as 94.8%. Moreover, the CMC value determined by the surface tensionmat was 63.1 mg L<sup>-1</sup>, i.e., 0.11 mM.

### 3.2. Effect of rhamnolipid on HCB solubilization and enhanced desorption

Fig. 1a indicates that HCB solubility increases linearly with the increase of rhamnolipid concentration (0.06–20 g L<sup>-1</sup>), consistent with previous results that a positive linear relationship was observed between HOCs solubilities and surfactants concentrations above CMC [5,25]. Furthermore, the molar solubilization ratio (MSR) is generally used to evaluate the solubilization effect of sur-



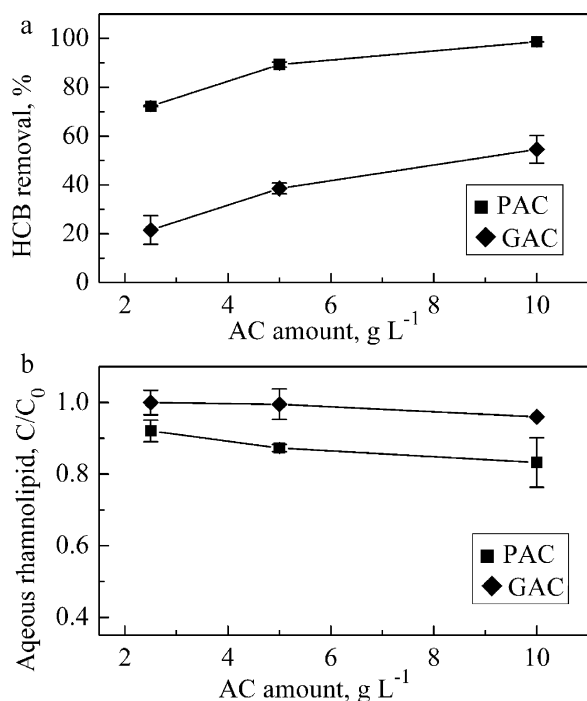
**Fig. 1.** Effect of rhamnolipid concentration on (a) HCB solubilization and (b) HCB desorption from kaolin.

factants which is defined as [25–27]

$$MSR = \frac{C_{HOC, mic} - C_{HOC, cmc}}{C_{surf} - CMC}$$

wherein  $C_{surf}$  is the surfactant concentration added (mol L<sup>-1</sup>), and  $C_{HOC, mic}$ ,  $C_{HOC, cmc}$  are the apparent solubilities of HOCs in surfactants solutions at concentration above CMC (i.e., micelles are formed) and at CMC (mol L<sup>-1</sup>), respectively. By using above equation, the MSR of rhamnolipid for HCB herein was calculated as  $5.4 \times 10^{-4}$ . In comparison, the value is lower than that of a nonionic surfactant, Tween 80 ( $1.72 \times 10^{-3}$  for HCB), while slightly higher than that of an anionic surfactant, SDS ( $3.7\text{--}4.7 \times 10^{-4}$  for HCB), according to the results of Kommalapati et al. [26]. Bordas et al. [25] also reported a lower MSR of a rhamnolipid mixture for pyrene compared with four selected nonionic chemical surfactants.

The effect of rhamnolipid dosage on HCB desorption from the spiked kaolin is shown in Fig. 1b. Generally, the fraction of HCB desorbed correlated positively with total rhamnolipid concentration in the range observed. Particularly, when 10 and 15 g L<sup>-1</sup> rhamnolipid solutions were used, the fractions of HCB desorbed were over 40% and 60%, respectively. Note that no appreciable HCB desorption was achieved for the first two rhamnolipid amounts (0.7 and 1.4 g L<sup>-1</sup>), although the total concentrations were above CMC (about 11 and 22 CMC, respectively). As well documented, only at an aqueous surfactant concentration above CMC (or a total surfactant concentration above effective CMC), enhanced desorption of HOCs from soils can be reached [4,5,8]. It can be found from Fig. 1b that only at total concentrations above 1.4 g L<sup>-1</sup>, the aqueous rhamnolipid is appar-



**Fig. 2.** (a) Adsorptive removal of HCB and (b) residual aqueous rhamnolipid in solution as an effect of AC dosage. Initial HCB 1.0 mg L<sup>-1</sup>, rhamnolipid 7.5 g L<sup>-1</sup>, time 6 h, pH 7.0.

ently higher than CMC, consistent with the aforementioned results of HCB desorption. The effective CMC herein (22 CMC) seems much higher than the reported value of 0.4 g L<sup>-1</sup> (12.1 CMC) by Bordas et al. [25]. The difference was probably associated with a much higher rhamnolipid adsorption capacity of kaolin due to a higher clay content relative to fine sand [8], and a much lower MSR of rhamnolipid for HCB than for pyrene ( $5.4 \times 10^{-4}$  versus  $7.5 \times 10^{-3}$ ). Moreover, inspection of Fig. 1b also suggests that fraction of aqueous rhamnolipid becomes increasingly abundant with the increase of total rhamnolipid concentration. By rearranging the results of rhamnolipid adsorption to kaolin to fit the Freundlich model, an equation of  $C_s = 0.104C_e^{0.40}$  ( $r^2 = 0.972$ ) could be obtained, which can well explain the increase in aqueous rhamnolipid fraction with total rhamnolipid concentration increasing. A nonlinear adsorption of rhamnolipid to soils was also reported by Mata-Sandoval et al. [8], wherein the Langmuir isotherm model was used to fit the adsorption of rhamnolipid to three soils.

### 3.3. Selective adsorption of HCB from rhamnolipid solution by ACs

The performances of selective adsorption of HCB from rhamnolipid solution by GAC and PAC are presented in Fig. 2. PAC showed a rather reliable removal efficiency of HCB in observed dosage range. Approximately 70% of HCB was adsorbed at a PAC amount of 2.5 g L<sup>-1</sup>, and the removal rose up to near 90% and 99% when 5 and 10 g L<sup>-1</sup> PAC were added, respectively. Comparatively, the HCB removal by GAC at the same dosage was much lower. Only 54% of HCB in rhamnolipid solution was removed at a GAC dosage of 10 g L<sup>-1</sup>. On the other hand, the loss of rhamnolipid due to adsorption by ACs should also be evaluated. Fig. 2b clearly shows that PAC exhibits a higher rhamnolipid adsorption relative to GAC. No significant surfactant loss was recorded for GAC for the observed dosage range of 2.5–10 g L<sup>-1</sup> (<5% loss at maximal GAC dosage). For PAC the loss was about 12% and 17% at PAC amounts of 5 and 10 g L<sup>-1</sup>, respectively. The differences in HCB removal and rhamnolipid loss between the two ACs were strongly correlated with the structure

**Table 3**

Single-point partition factor for HCB ( $K_d$ ), rhamnolipid ( $K_d^*$ ) and the selectivity ( $S$ ) of PAC at various conditions.

Parameters	$K_d$	$K_d^*$	$S$
PAC amount, g L <sup>-1</sup>			
2.5	1043.2	34.5	30.3
5	1672.6	29.2	57.3
10	3847	23.3	165.1
GAC amount g L <sup>-1</sup>			
2.5	109.9	0.14	769.2
5	125.5	1	124.1
10	120.2	4.2	28.8
Rhamnolipid concentration, g L <sup>-1</sup>			
3.3	4654.3	22.3	209.3
7.5	2507.1	17	147.5
15	1126.8	12.8	88
20	448.1	7.7	57.9

characteristics of ACs. Particularly, the BET specific surface area and the pore volume of PAC are almost as 1.9 and 1.8 times as GAC, respectively, both of which play principal roles in the adsorption capacity for organics [19,28].

The selectivity ( $S$ ) proposed by Ahn et al. [19,20,29] can be employed here to evaluate the performances of selective removal of HCB by two ACs, which is defined as

$$S = \frac{K_d}{K_d^*} = \frac{C_s C_e^*}{C_e C_s^*}$$

wherein  $K_d$ ,  $K_d^*$  are the single-point partition coefficients of HCB and rhamnolipid between ACs and solutions, respectively.  $C_s$  (mg kg<sup>-1</sup>),  $C_s^*$  (g kg<sup>-1</sup>) represent HCB and rhamnolipid concentrations in ACs, and  $C_e$  (mg L<sup>-1</sup>),  $C_e^*$  (g L<sup>-1</sup>) represent the aqueous HCB and rhamnolipid concentrations. Moreover,  $K_d = C_s/C_e$ ,  $K_d^* = C_s^*/C_e^*$ . By using above equation,  $K_d$ ,  $K_d^*$  and  $S$  for PAC and GAC were calculated and listed in Table 3. It is suggested that both  $K_d$  and  $K_d^*$  values for PAC are almost one order of magnitude larger than those for GAC, in tune with the results depicted in Fig. 1. Decreasing  $K_d$  and  $K_d^*$  values with increasing AC sizes was also reported by Ahn et al. [19]. In addition, all  $S$  values for PAC and GAC were much larger than 1, which meant reliable selectivity could be achieved by two ACs. However, inspection of Table 3 suggests that the selectivity cannot be the sole measure to select AC and its amounts. The highest  $S$  value was found for GAC at 2.5 g L<sup>-1</sup>, which was caused primarily by the lowest rhamnolipid adsorption, while in fact only 25% of HCB removal was reached. As a result, considering  $S$  and HCB removal simultaneously would be more appropriate. In this sense, PAC at 10 g L<sup>-1</sup> possessed both a high  $S$  value (165) and HCB removal (99%), was thus selected for the following studies.

To further verify the availability of PAC on selective removal of HCB and the potential of rhamnolipid reuse, the effects of initial rhamnolipid concentration on the selectivity were investigated. It is indicated in Fig. 3 that an increase in initial rhamnolipid concentration gives rise to a decreased HCB removal and rhamnolipid adsorptive loss. The reduced HCB removal was not unexpected, since higher surfactant concentrations meant higher HCB solubilization effect or directly, stronger partitioning capacity of the solution. The decline in the fraction of aqueous rhamnolipid, however, was probably relevant to the increasingly saturated adsorption of rhamnolipid considering limited adsorption sites of PAC and excess rhamnolipid content relative to PAC dosage. Furthermore, the decreasing selectivity suggests that higher rhamnolipid concentration affects the selective adsorption process adversely (Table 3).



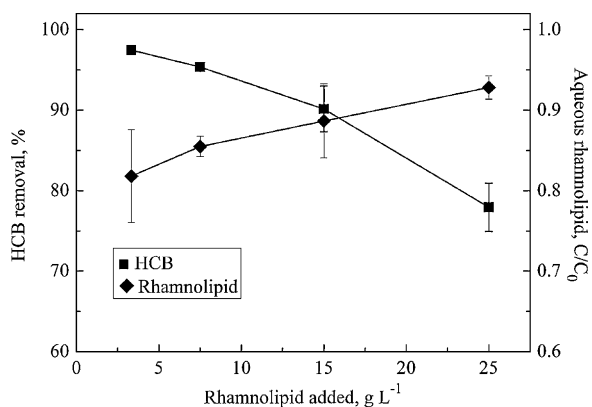


Fig. 3. Effect of initial rhamnolipid concentration on selective adsorption of HCB by PAC. PAC dosage 10 g L<sup>-1</sup>, time 6 h, pH 7.0. Initial HCB 1 mg L<sup>-1</sup>.

### 3.4. Enhanced remediation of HCB-contaminated soils by soil washing coupled with AC adsorption

The feasibility of coupling PAC selective adsorption with rhamnolipid-enhanced soil washing was tested. As displayed in Fig. 4a, when 12.5 g L<sup>-1</sup> rhamnolipid solution was employed, HCB removal from kaolin and real soil both declined dramatically as the cycles of washing increased. For instance, the HCB removal was 47% for real soil in SW1, while the efficiency dropped down to less than

15% in SW3. For the adsorption of HCB in rhamnolipid solution by PAC, the removal were all nearly complete (>98%) for both soils in two adsorption treatments (AC1 and AC2). Comparatively, the performance seemed more encouraging when 25 g L<sup>-1</sup> rhamnolipid solution was used (Fig. 4b). A total of 67% and 71% of HCB were washed out for kaolin and real soil in SW1, which were as 1.3 and 1.5 times as those for kaolin and real soil at rhamnolipid concentration of 12.5 g L<sup>-1</sup>, respectively. Moreover, only a slight decrease in HCB leaching was observed in the following SW2 and SW3 for either kaolin or real soil. The leaching percentages of HCB from soils in SW3 were reduced by 12% and 13% compared with SW1 for the two soils, respectively. Furthermore, approximately 89% adsorptive removal of HCB was achieved in AC1, and the efficiencies grew up slightly to 94% and 91% for washing solutions from kaolin and real soil, probably due to a lowering rhamnolipid concentration via adsorption to soils in SW2. Noteworthy that the overall HCB removal of near 90% by 10 g L<sup>-1</sup> PAC is acceptable, given the consideration that a further increase in HCB removal means a higher dosage of PAC and a higher loss of rhamnolipid. Interestingly, an approximately 90% adsorption of pyrene by AC was also proposed as a good goal according to a mathematical evaluation by Ahn et al. [19].

The variations of aqueous rhamnolipid concentration after each step of soil washing or AC adsorption are illustrated in Fig. 4c–d. An almost linear decrease in aqueous rhamnolipid concentration was recorded for either kaolin or real soil when 12.5 g L<sup>-1</sup> biosurfactant was applied (Fig. 4c). After two cycles of soil washing and

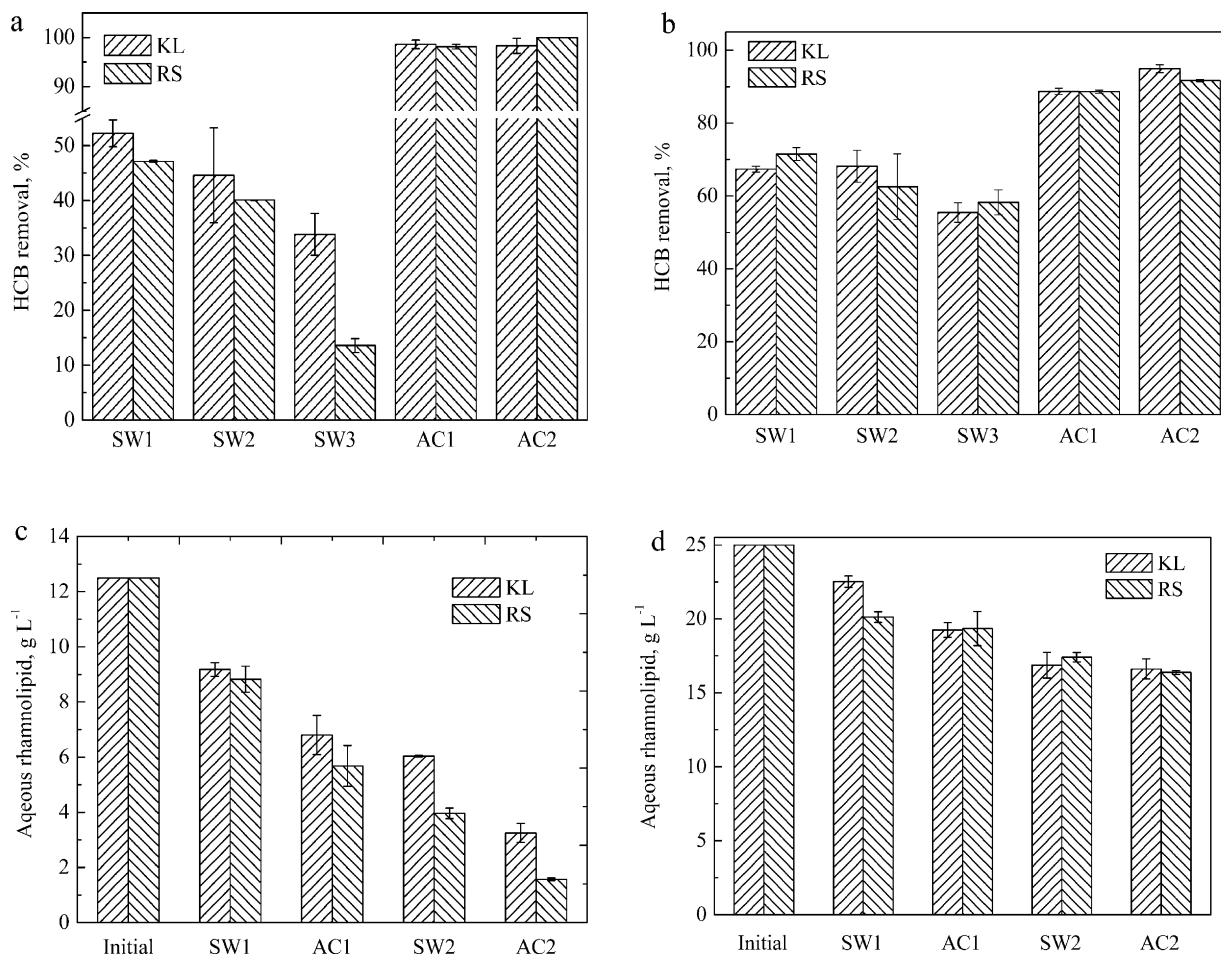
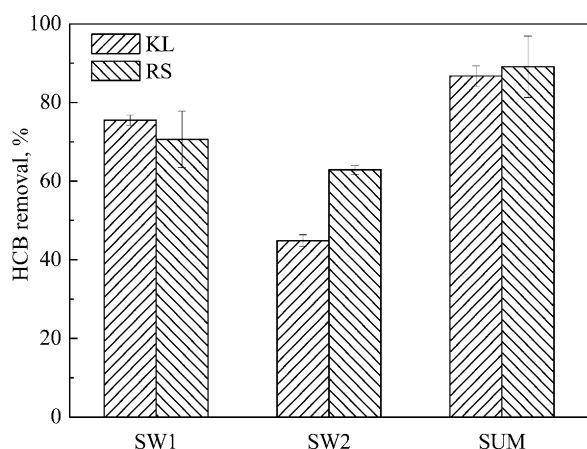


Fig. 4. Performance of combined soil washing-PAC adsorption process in successive washing of kaolin (KL) and real soil (RS): HCB removal at rhamnolipid concentrations of (a) 12.5 and (b) 25 g L<sup>-1</sup>, and variation of aqueous rhamnolipid at initial concentrations of (c) 12.5 and (d) 25 g L<sup>-1</sup>. Washing time 48 h, adsorption time 6 h, PAC 10 g L<sup>-1</sup>, pH 7.0.



**Fig. 5.** Repeated washing of kaolin and real soil by soil washing-PAC adsorption combined process. Rhamnolipid  $25 \text{ g L}^{-1}$ , PAC  $10 \text{ g L}^{-1}$ , pH 7.0.

AC adsorption, the residual concentrations of aqueous rhamnolipid were about  $3.2$  and  $2.0 \text{ g L}^{-1}$  for kaolin and real soil, respectively. This dramatical loss of aqueous rhamnolipid (due to adsorption to soil matrix and PAC) was the main reason for decreased HCB washing efficiency in Fig. 4a. In comparison, the rhamnolipid concentration was lower for real soil than for kaolin at all stages of processing, in accordance with the leaching of HCB from two soils (Fig. 4a). As for the remediation using  $25 \text{ g L}^{-1}$  rhamnolipid solution, a gradual reduction in aqueous rhamnolipid was evidenced (Fig. 4d). After four steps of processing, the residual biosurfactant concentrations were as high as  $16 \text{ g L}^{-1}$  for both soils, which accounted for over 64% of the initial concentration. The high contents of rhamnolipid also explained the incomplete adsorptive removal of HCB for AC1 and AC2 in Fig. 4b. Note that the less adsorptive loss of biosurfactant with higher initial concentrations ( $25$  versus  $12.5 \text{ g L}^{-1}$ ) was somewhat consistent with aforementioned observations, i.e., an increased initial rhamnolipid concentration gave rise to a decreased fraction of rhamnolipid adsorbed by either kaolin (Section 3.2) or GAC (Section 3.3 and Fig. 3). As a result, it is suggested that for the combined soil washing-AC adsorption process, higher concentrations of surfactants would be more cost-efficient. However, considering a reduced HCB adsorption (or a higher dose of PAC required) at higher rhamnolipid contents, a properly high dosage of rhamnolipid is suggested.

The combined soil washing-AC adsorption technique was further evaluated as washing the same portion of soils repeatedly to achieve a desirable overall HCB removal. It can be seen from Fig. 5 that SW2 could leach 45–63% of the residual HCB in soils from SW1 (if measured by the initial HCB contents in kaolin and real soil, the leaching will be 11.3% and 18.5%). More appealing, the overall HCB removal by two cycles of washing were 87% and 89% for kaolin and real soil, and the final adsorptive losses of rhamnolipid (subjected to SW1–2 and AC1) were less than 25% (data not shown). As a result, the rhamnolipid solution could be further regenerated by PAC and used to wash another portion of soils.

Note that after a series of soil washing-AC adsorption treatments, rhamnolipid concentration may decrease to an unfavorable extent, i.e., insufficient for further soil washing. At these circumstances, the capability of the rhamnolipid washing solution can be restored by adding a new portion of rhamnolipid at appropriate intervals. Moreover, recovery of rhamnolipid from above “deficient” solution can be also reached by simply acidifying the solution to precipitate rhamnolipid and re-dissolving the solid for further use. It should also be mentioned that for a full-scaled treatment of HOCs-contained rhamnolipid (or other surfactants) washing solutions by PAC selective adsorption, microfiltration/ultrafiltration

may be used (alone or after centrifugation) to separate PAC from rhamnolipid solution. In Addition, other mixing methods such as pumping the soil washing solutions through PAC-packed columns could be applied to avoid the need of separation. The spent PAC, meanwhile, can be regenerated via thermal or microwave methods and then reused for soil washing solution treatment.

#### 4. Conclusions

The present study investigates the performance of PAC on selective adsorption of HCB from biosurfactant rhamnolipid solution. The feasibility of rhamnolipid-enhanced soil washing coupled with PAC adsorption was further verified. Main observations and conclusions can be summed up as follows:

- (1) Rhamnolipid showed a reliable solubilization effect on HCB, the MSR was calculated as  $5.4 \times 10^{-4}$ , slightly higher than the reported value of SDS for HCB. Significant enhanced desorption of HCB from kaolin was also evidenced, over 60% of HCB could be removed by using  $15 \text{ g L}^{-1}$  rhamnolipid solution. The fraction of aqueous rhamnolipid was found increasing with increased biosurfactant added.
- (2) Compared with GAC, PAC was more efficient to remove HCB from rhamnolipid solution. By using  $10 \text{ g L}^{-1}$  PAC, 99% of HCB adsorption was achieved, with an acceptable rhamnolipid loss of 17%. Furthermore, an increase in initial rhamnolipid concentration led to a decrease in HCB removal and adsorptive loss of rhamnolipid.
- (3) The successive PAC adsorption-soil washing process achieved encouraging leaching of HCB from kaolin and real soil by using  $25 \text{ g L}^{-1}$  rhamnolipid as a washing solution and  $10 \text{ g L}^{-1}$  PAC as an adsorbent. The individual HCB removal from soils was 55–71% for three cycles of washing, and the adsorption of HCB by PAC was nearly 90%. In addition, the adsorptive loss of aqueous rhamnolipid to soils and PAC was about 35% after three washing and two adsorption treatments. The combined soil washing-AC adsorption process was also testified effective to remove 86–88% of HCB from both soils by washing the same sample for twice. Therefore, it is suggested that biosurfactants-enhanced soil washing coupled with AC adsorption is a promising alternative to remediate soils contaminated with HOCs.

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#### References

- [1] S. Deshpande, B.J. Shiao, D. Wade, D.A. Sabatini, J.H. Harwell, Surfactant selection for enhancing ex-situ soil washing, *Water Res.* 33 (1999) 351–360.
- [2] C.N. Mulligan, R.N. Yong, B.F. Gibbs, Surfactant-enhanced remediation of contaminated soil: a review, *Eng. Geol.* 60 (2001) 371–380.
- [3] R. Zhang, P. Somasundaran, Advances in adsorption of surfactants and their mixtures at solid/solution interfaces, *Adv. Colloid Interface Sci.* 123 (2006) 213–229.
- [4] S.O. Ko, M.A. Schlautman, E.R. Carraway, Partitioning of hydrophobic organic compounds to sorbed surfactants. I. Experimental studies, *Environ. Sci. Technol.* 32 (1998) 2769–2775.
- [5] K. Yang, L.Z. Zhu, B.S. Xing, Enhanced soil washing of phenanthrene by mixed solutions of TX100 and SDBS, *Environ. Sci. Technol.* 40 (2006) 4274–4280.

- [6] W. Zhou, L. Zhu, Enhanced soil flushing of phenanthrene by anionic–nonionic mixed surfactant, *Water Res.* 42 (2008) 101–108.
- [7] W.H. Noordman, W. Ji, M.L. Brusseau, D.B. Janssen, Effects of rhamnolipid biosurfactants on removal of phenanthrene from soil, *Environ. Sci. Technol.* 32 (1998) 1806–1812.
- [8] J.C. Mata-Sandoval, J. Karns, A. Torrents, Influence of rhamnolipids and Triton X-100 on the desorption of pesticides from soils, *Environ. Sci. Technol.* 36 (2002) 4669–4675.
- [9] C.N. Mulligan, Environmental applications for biosurfactants, *Environ. Pollut.* 133 (2005) 183–198.
- [10] Y. Asci, M. Nurbas, Y.S. Acikel, A comparative study for the sorption of Cd(II) by soils with different clay contents and mineralogy and the recovery of Cd(II) using rhamnolipid biosurfactant, *J. Hazard. Mater.* 154 (2008) 663–673.
- [11] L.Z. Zhu, M. Zhang, Effect of rhamnolipids on the uptake of PAHs by ryegrass, *Environ. Pollut.* 156 (2008) 46–52.
- [12] L.M.S. Anna, A.U. Soriano, A.C. Gomes, E.P. Menezes, M.L.E. Gutarra, D.M.G. Freire, N. Pereira, Use of biosurfactant in the removal of oil from contaminated sandy soil, *J. Chem. Technol. Biotechnol.* 82 (2007) 687–691.
- [13] S. Berselli, G. Milone, P. Canepa, D. Di Gioia, F. Fava, Effects of cyclodextrins, humic substances, and rhamnolipids on the washing of a historically contaminated soil and on the aerobic bioremediation of the resulting effluents, *Biotechnol. Bioeng.* 88 (2004) 111–120.
- [14] C.Z. Cui, C. Zeng, X. Wan, D. Chen, J.Y. Zhang, P. Shen, Effect of rhamnolipids on degradation of anthracene by two newly isolated strains, *Sphingomonas* sp. 12A and *Pseudomonas* sp. 12B, *J. Microbiol. Biotechnol.* 18 (2008) 63–66.
- [15] R.D. Villa, A.G. Trovo, R.F.P. Nogueira, Soil remediation using a coupled process: soil washing with surfactant followed by photo-Fenton oxidation, *J. Hazard. Mater.* 174 (2010) 770–775.
- [16] D. Fabbri, A.B. Prevot, V. Zelano, M. Ginepro, E. Pramauro, Removal and degradation of aromatic compounds from a highly polluted site by coupling soil washing with photocatalysis, *Chemosphere* 71 (2008) 59–65.
- [17] D. Fabbri, A. Crime, M. Davezza, C. Medana, C. Baiocchi, A.B. Prevot, E. Pramauro, Surfactant-assisted removal of sweep residues from soil and photocatalytic treatment of the washing wastes, *Appl. Catal. B: Environ.* 92 (2009) 318–325.
- [18] J. Gomez, M.T. Alcántara, M. Pazos, M.A. Sanroman, Remediation of polluted soil by a two-stage treatment system: desorption of phenanthrene in soil and electrochemical treatment to recover the extraction agent, *J. Hazard. Mater.* 173 (2010) 794–798.
- [19] C.K. Ahn, Y.M. Kim, S.H. Woo, J.M. Park, Selective adsorption of phenanthrene dissolved in surfactant solution using activated carbon, *Chemosphere* 69 (2007) 1681–1688.
- [20] C.K. Ahn, M.W. Lee, D.S. Lee, S.H. Woo, J.M. Park, Mathematical evaluation of activated carbon adsorption for surfactant recovery in a soil washing process, *J. Hazard. Mater.* 160 (2008) 13–19.
- [21] J.Z. Wan, S.H. Yuan, K.T. Mak, J. Chen, T.P. Li, L. Lin, X.H. Lu, Enhanced washing of HCB contaminated soils by methyl-beta-cyclodextrin combined with ethanol, *Chemosphere* 75 (2009) 759–764.
- [22] W. Shen, X.K. Li, S.L. Yang, C.F. Ning, Identification of rhamnolipids produced by *Pseudomonas* sp. BS203 with electrospray ionization-mass spectrometry, *Chin. J. Anal. Chem.* 34 (2006) 69–72.
- [23] Y.M. Zhang, R.M. Miller, Enhanced octadecane dispersion and biodegradation by a *Pseudomonas* rhamnolipid surfactant (biosurfactant), *Appl. Environ. Microbiol.* 58 (1992) 3276–3282.
- [24] F.J. Ochoa-Loza, W.H. Noordman, D.B. Janssen, M.L. Brusseau, R.M. Maier, Effect of clays, metal oxides, and organic matter on rhamnolipid biosurfactant sorption by soil, *Chemosphere* 66 (2007) 1634–1642.
- [25] F. Bordas, P. Lafrance, R. Villemur, Conditions for effective removal of pyrene from an artificially contaminated soil using *Pseudomonas aeruginosa* 57S rhamnolipids, *Environ. Pollut.* 138 (2005) 69–76.
- [26] R.R. Kommalapati, K.T. Valsaraj, W.D. Constant, D. Roy, Aqueous solubility enhancement and desorption of hexachlorobenzene from soil using a plant-based surfactant, *Water Res.* 31 (1997) 2161–2170.
- [27] D. Roy, R.R. Kommalapati, S.S. Mandava, K.T. Valsaraj, W.D. Constant, Soil washing potential of a natural surfactant, *Environ. Sci. Technol.* 31 (1997) 670–675.
- [28] Y. Fan, B. Wang, S. Yuan, X. Wu, J. Chen, L. Wang, Adsorptive removal of chloramphenicol from wastewater by NaOH modified bamboo charcoal, *Bioresour. Technol.* 101 (2010) 7661–7664.
- [29] C.K. Ahn, S.H. Woo, J.M. Park, Enhanced sorption of phenanthrene on activated carbon in surfactant solution, *Carbon* 46 (2008) 1401–1410.