Partitioning of hexachlorobenzene in a kaolin/humic acid/surfactant/water system: Combined effect of surfactant and soil organic matter

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ABSTRACT

Understanding the combined effect of soil organic matter (SOM) and surfactants on the partitioning of hydrophobic organic compounds in soil/water systems is important to predict the effectiveness of surfactant-enhanced remediation (SER). In the present study we investigate the partitioning of hexachlorobenzene (HCB) within a humic acid (HA)-coated kaolin/Triton X-100 (TX100)/water system, with special emphasis on the interaction between TX100 and HA, and their combined effect on HCB sorption. HA firstly enhanced then suppressed TX100 sorption to kaolin as the amounts of HA increased, while the addition of TX100 led to a consistent reduction in HA sorption. In the HA-coated kaolin/TX100/water system, TX100 played a primary role in enhancing desorption of HCB, while the role could be suppressed and then enhanced as HA coating amounts increased. Only at HA coating above 2.4%, dissolved HA outcompeted clay-bound HA for HCB partitioning, resulting in dissolved HA enhanced desorption. The presence of dissolved HA at these conditions further promoted the effectiveness of TX100 enhanced desorption. Despite a reduced TX100 sorption to clay was achieved due to the presence of dissolved HA, the effect on HCB desorption was comparatively slight. A reliable cumulative influence of HA and TX100 on HCB desorption was observed, although HCB desorption by HA/TX100 mixed was less than the sum of HA and TX100 individually. Our study suggests that for soils of high organic contents, the combined effect of SOM and surfactants on HOCs desorption can be applied to improve the performance of SER.

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1. Introduction

Surfactant-enhanced remediation (SER) has been proposed as an efficient clean-up technology for soils contaminated with hydrophobic organic compounds (HOCs) [1–3]. Surfactants can hypothetically remediate soils by incorporating HOCs molecules into hydrophobic micelles and enhancing the desorption (i.e., mobility or availability) of HOCs from soils [4]. Soil organic matter (SOM), a ubiquitous substance and also an important part of soil, greatly affects the SER process. SOM not only governs the mobility of HOCs in soils but also contributes to the adsorption of surfactants to soils [5–8]. Therefore, SOM imposes an adverse effect on SER due to its strong sorptive affinity for HOCs and surfactants. The dissolved fraction of SOM (DOM), however, is capable of mobilizing HOCs in soils [9,10]. As a consequence, the interaction between surfactants and SOM/DOM in soil/water systems makes the partitioning behaviors of HOCs more complex in SER process.

Very recently the combined effect of surfactants and DOM on HOCs dissolution was investigated. Cho et al. [11] found that the apparent solubilities of naphthalene, phenanthrene and pyrene in a Triton X-100 (TX100) and DOM mixed solution were nearly the sum of those in TX100 and DOM solution alone. On the contrary, obvious reduction of HOCs solubilities were recorded when DOM was added to sodium dodecyl sulfate (SDS) solution (with SDS concentration below critical micelle concentration (CMC)) [11,12]. However, present knowledge about the HOCs dissolution behaviors in surfactant-DOM mixed solutions may not necessarily be applicable to predict the mobility of the contaminants in soil/water systems. Cheng and Wong [13] found that the desorption of phenanthrene and pyrene from soils by Tween 80-DOM mixed solutions was more than the sum of Tween 80 and DOM alone, different from above results of HOCs dissolution by Cho et al. [11]. The authors attributed this synergistic effect (i.e., the PAH desorption by DOM and Tween 80 being more than additive) to possible formation of DOM-surfactant complexes that might possess a stronger desorbing capacity for PAHs [13]. However, we suggest that above results may be also relevant to the complex sorptive interactions between Tween 80 and DOM in soil/water systems. To be more specific, SOM may affect the adsorption of

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surfactants to soils dually (i.e., the soil-bound SOM increased the surfactant adsorption while the DOM decreased), and similar for the effect of surfactants on DOM sorption. In other words, other than the interactions between aqueous surfactants and DOM (e.g., the formation of DOM-surfactant complexes), the influence of surfactant-DOM interactions on surfactant and DOM adsorption to soils may also influence the partitioning of HOCs in soil–water systems. Therefore, a deeper insight into this interaction is essential to further verify the combined effect of surfactants, SOM, and DOM on HOCs adsorption in soil/water systems, and to better understand SER.

In the present study we investigated the partitioning of hexachlorobenzene (HCB), used here as a representative HOC, in a HA-coated kaolin (HACK)/water system in the presence of TX100. TX100 was chosen as the representative surfactant since it is commonly selected in studies for soil remediation. Purified commercial HA was used as the representative SOM fraction. Our objectives were: (1) to investigate the influence of TX100-SOM interaction on TX100 and DOM sorption to clay, and the resultant effect on HCB partitioning; (2) to study the combined effect of SOM and TX100 on HCB sorption; (3) to illustrate contributions of surfactants, SOM, DOM to HCB sorption in a complicated HACK/surfactant/water system.

2. Materials and methods

2.1. Chemicals, HA and kaolin

HCB (99.0%) was purchased from Shanghai General Reagent Factory, China. TX100 (>99.0%) was from Aldrich and used as received. Hexane, sodium chloride, and hydrochloric acid were all of analytical purity. Deionized water (>18.0 mΩ) was used for solution preparation and dilution.

Commercial HA powder was obtained from Lemandou Chemicals Co., Ltd., China, which was derived from lignite (Sinkiang, China). The HA was further purified according to the procedures recommended by the International Humic Substances Society (IHSS) before use [14]. The element composition of the purified HA was analyzed on a Vario Micro element analyzer (Elementar, Germany). The HA comprises 48.3% C, 2.6% H, 29.3% O, 1.1% N, and 0.3% S.

Kaolin (chemical purity) obtained from Shanghai Qingpu Chemical CO. Ltd. was selected as the model clay. The organic content of kaolin was 0.12%, and the cation exchange capacity (CEC) measured by $BaCl_2–H_2SO_4$ method (ISO 11260-1997) was 16.9 cmol kg^{-1}. The BET specific surface area measured by a surface area apparatus (Micromeritics Tristar 3000) was 19.4 m^2 g^{-1}. X-ray fluorescence analysis (Genesis, EDAX Inc.) shows that its main mineral elements were Si (59.9% in wt) and Al (36.7%). Other physicochemical properties associated with the kaolin are listed as Table S1 in Supplementary Materials.

2.2. Influence of HA–TX100 interaction on HA and TX100 sorption to kaolin

All the sorption experiments were carried out in triplicate using batch equilibrium technique in glass vials sealed with Teflon screw caps. Data processing and fitting (including isotherm model fitting) were performed using Origin v. 8.0.

To begin with, the sorption of HA or TX100 in a kaolin/water system was studied respectively. A total of 0.5 g kaolin was mixed with 10 mL HA (0–2500 mg L^{-1}) or TX100 solutions (0–10 mmol L^{-1}). The vials were agitated in a reciprocating shaker end over end for 48 h (25 ± 1 °C), and centrifuged at 4000 rpm for 10 min. The supernatant was filtered through a 0.45 μm cellulose acetate membrane and subjected for HA or TX100 analysis.

The influence of HA–TX100 interaction on TX100 and HA sorption to kaolin was further investigated in two different manners (0.5 g kaolin in 10 mL solutions): with constant HA total concentration of 400 mg L^{-1} and varying TX100 total concentrations of 0–10 mmol L^{-1}, or with constant TX100 total concentration of 2 mmol L^{-1} and varying HA total concentrations of 0–2500 mg L^{-1}. The pH of the slurries was adjusted to 7.0 ± 0.2 with appropriate concentrations of HCl or NaOH (mostly 1 mol L^{-1} while 10 mol L^{-1} HCl or NaOH was used for samples with high HA concentrations). Furthermore, 0.01 mol L^{-1} NaCl was contained as the background electrolyte. Equilibrium aqueous concentrations of HA and TX100 were both analyzed for each sample.

2.3. Influence of HA or TX100 on HCB sorption to kaolin

In this section firstly the influence of HA addition on HCB sorption to kaolin was investigated. A total of 0.5 g kaolin was mixed with 10 mL HA solutions (0–2500 mg L^{-1}, final pH 7). Then 40 μL of HCB acetone solution was added into the vials by a microsyringe before shaking (acetone fraction was below 0.5%). The total concentration of HCB was 0.5 mg L^{-1} (or 10 mg kg^{-1} kaolin). After equilibrium and centrifugation, the supernatant was filtered through a 0.45 μm cellulose acetate membrane. HCB in the supernatant was then extracted by hexane via liquid-liquid extraction in 11-mL glass vials (with an extraction ratio of 1:2, agitated in a shaker for 2 h) and analyzed by gas chromatography (GC). Meanwhile HA in the filtrate was measured.

Secondly, the influence of TX100 on HCB sorption was investigated which followed the same procedure as described above. TX100 concentration used was 0–10 mmol L^{-1}. Both TX100 and HCB equilibrium concentrations were determined for each sample.

### 2.4. HCB partitioning in a solid HA/TX100/water system

Predetermined volumes of HA and TX100 stock solutions (HA 5 g L^{-1} and TX100 20 mmol L^{-1}) were pipetted into 50 mL glass flasks, and diluted with deionized water to 20 mL. The amounts of HA added were as 0–2.5 g L^{-1}, and the total TX100 concentration was 2 mmol L^{-1}. The pH of the mixture was adjusted to 2–3 with HCl to precipitate HA thoroughly. Then 80 μL HCB acetone solution was added before shaking. The total concentration of HCB was 0.5 mg L^{-1}. After equilibrium and centrifugation, the supernatant was filtered through a 0.45 μm cellulose acetate membrane and subjected for TX100 and HCB analysis.

2.5. HCB partitioning in a HACK/TX100/water system

The sorption of HCB to HACK (detailed preparation procedures are provided in Supplementary Materials) in the presence of TX100 was further investigated. A total of 0.5 g HACK with varied HA coating amounts (0.25–5%) was mixed with 10 mL TX100 solutions (0–10 mmol L^{-1}). The pH of the slurry was then adjusted to 7.0 ± 0.2 or 3.0 ± 0.2 (pH 3.0 could avoid HA dissolution from HACK, thereby better reveal the role of solid HA in the partitioning of TX100 and HCB). Then 40 μL HCB acetone solution was added into the vials by a micro-syringe before shaking (the final acetone fraction was below 0.5%). Both TX100 and HCB equilibrium concentrations were determined for each sample.

2.6. Chemical analysis

Aqueous TX100 was analyzed by a high performance liquid chromatography (Hitachi L7100, Japan) equipped with an
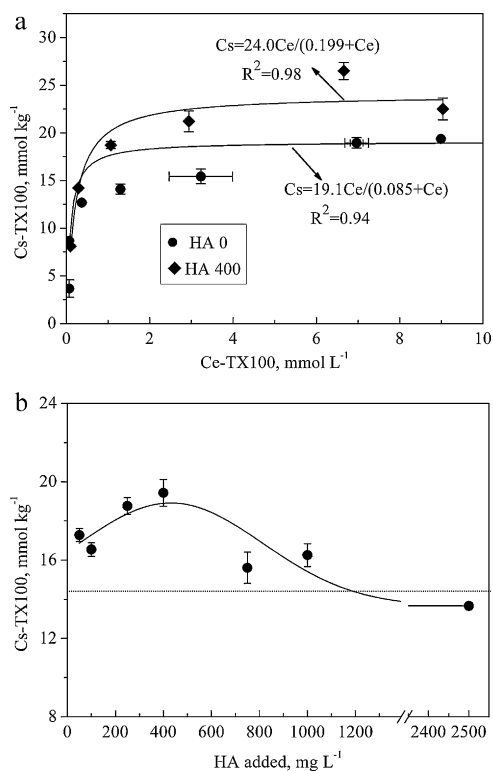
Fig. 1. (a) TX100 sorption isotherm at 0 and 400 mg L^{-1} HA; (b) influence of HA amount on TX100 (2 mmol L^{-1}) sorption to kaolin.

L-7420 ultraviolet–visible (UV–vis) detector and an Agilent ZOR-BAX Eclipse XDB-C18 column (Agilent, USA). The wavelength was set at 223 nm. The mobile phase was 90% methanol plus 10% water, with a flow rate of 1.0 mL min^{-1}. 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 [15].

The aqueous concentration of HA was measured by a Cary 50 UV–vis spectrophotometer (Varian, USA) at 254 nm (although TOC analysis is frequently used to quantify the humic substances (including HA), herein the co-presence of TX100 especially above 2 mmol L^{-1} may seriously interfere the TOC analysis of HA. However, a much higher absorptivity of HA under UV-254 than TX100 suggest that the spectrophotometer measurement might be more appropriate). The linear range of the HA working curve was 0–24 mg L^{-1} ($r = 0.9999$). The absorbance of HA in the absence of TX100 can be obtained directly. Based on the preliminary observation that the absorbance of TX100 and HA mix at 254 nm was additive, HA content could be deduced by subtracting the absorbance contributed by TX100 from the absorbance of the TX100-HA mixture (the absorbance of TX100 can be calculated from its working curve at 254 nm and the corresponded concentration obtained by HPLC).

3. Results and discussion

3.1. Effects of SOM on TX100 sorption in a kaolin–water system

Fig. 1a displays the sorption isotherms of TX100 in the absence and presence of HA (400 mg L^{-1}) in a kaolin/water system. The two isotherms can be well fitted by the Langmuir model in the range of 0–10 mmol L^{-1}, similar to those reported in the literature [7,16]. Comparison of the maximal sorption amounts of TX100 between HA and HA-free systems (24.0 vs 19.1 mmol kg^{-1}) indicates that

the presence of HA at 400 mg L^{-1} increased the sorption of TX100. Enhanced sorption of surfactant to soil as an effect of SOM has been reported by a number of researchers [17–19]. Zhu et al. [20] revealed that the sorption capacity of HA for TX100 was almost one order larger than that of kaolin. Zhang et al. [21] also reported that much higher sorption capacity and partitioning coefficient (K_d) for TX100 was exhibited by HA relative to original soil.

Furthermore, as shown in Fig. 1b, for the observed HA concentration range, the sorption of TX100 firstly increased and then decreased, with a maximum at HA concentration of about 400 mg L^{-1}. The initial increase in TX100 sorption was strongly correlated with the partitioning of surfactant to the clay-bound HA. However, as the added HA increased above 400 mg L^{-1}, the amount and more importantly, the fraction of the dissolved HA increased considerably (as indicated by decreasing K_d values in Table S2). The dissolved HA may compete with the clay-bound HA for the partitioning of TX100, since HA molecule contains both hydrophilic and hydrophobic structure, very similar to surfactants. Another explanation may be that the dissolved HA could reduce the TX100 adsorption by forming HA–TX100 complexes, similar to the complexing of HOCs to DOM [10,22,23]. Lee et al. [22] found that the sorption isotherm of TX100 to a Florida peat was of a skewed-Gaussian shape, with a sharp decrease in TX100 sorption coefficient at equilibrium concentration above 1000 mg L^{-1}. It was suggested that at higher TX100 concentrations, more SOM was dissolved, and the DOM was expected to promote the "dissolution" of TX100 and reduce the probability of TX100 sorption [22].

Inspection of Fig. 1b further reveals that even at relatively high concentrations of dissolved HA (100–400 mg L^{-1}), the sorption of TX100 was higher than sorption at HA = 0, suggesting a considerable binding of TX100 to the kaolin-bound HA. It can be also estimated from Fig. 1b that the critical HA amount when the dissolved HA outcompeted the clay-bound fraction for TX100 partitioning was approximately 1500 mg L^{-1}. As a result, it is expected that the effect of SOM on the sorption of nonionic surfactants is dependent on the content of SOM, and only at content high enough as to induce a significant amount of DOM, SOM can reduce the sorption of surfactants, thereby functioning positively to SER.

3.2. Effects of TX100 on HA sorption in a kaolin/water system

The partitioning of HA within a kaolin/water system is presented as Fig. 2a. The sorption isotherm of HA in the TX100-free system can be described as a two phase linear relationship: with a steep increase for dissolved HA concentration of 0–7 mg L^{-1} and a followed slowing increase in the range of 7–360 mg L^{-1}. Moreover, a linear regression can be applied for HA sorption in the presence of TX100 when the aqueous concentration of HA ranged from 29 to 610 mg L^{-1}. Inspection of Fig. 2a reveals that the copresence of TX100 at 2 mmol L^{-1} decreased HA sorption to kaolin. Furthermore, the slope of HA isotherm in the presence of TX100 is lower than the HA isotherm in the absence of TX100 (5.7 vs 7.7), suggesting an increased reduction in HA sorption as the dissolved HA increases.

Additionally, Fig. 2b shows a consistent decrease in HA sorption with an increase of TX100 concentration (0–8 mmol L^{-1}). In particular, the presence of 8 mmol L^{-1} TX100 could reduce the sorption of HA by 38% compared with TX100-free system. Similar observations were also recorded by Cheng and Wong [13], therein the presence of Tween 80 at 150 mg L^{-1} dramatically reduced the sorption of DOM to soil. Preferential binding of Tween 80 molecules to soil with respect to DOM was hypothesized to be relevant to the above results [13]. Despite the lower calculated partitioning coefficients for TX100 (2–34 L kg^{-1} at 1–10 mmol L^{-1}, Table S1) in comparison with HA (23.5–80 L kg^{-1} at 350–1000 mg L^{-1}, Table S1), it may still be reasonable to suggest that the competitive
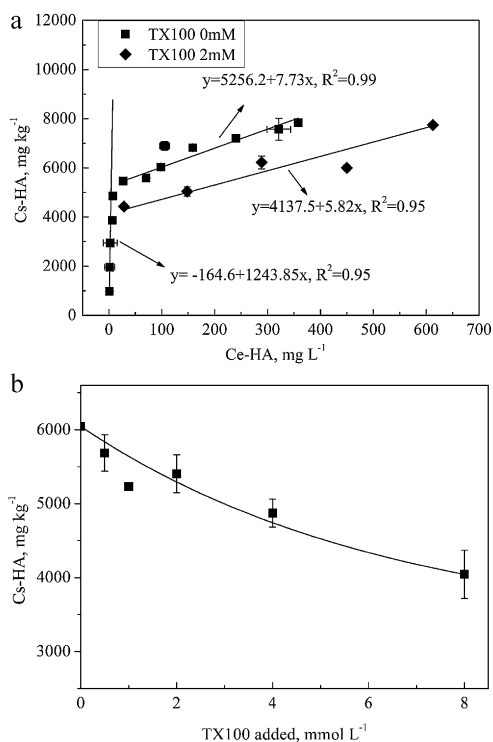
Fig. 2. (a) HA sorption isotherm at 0 and 2 mmol L^{-1} TX100; (b) influence of TX100 concentration on HA (400 mg L^{-1}) sorption to kaolin.

Fig. 3. Influence of (a) HA and (b) TX100 on HCB sorption to kaolin individually. HCB 0.5 mg L^{-1}, pH 7.0.

adsorption between the two molecules to the clay surface contributed primarily to the declined sorption of HA as the aqueous TX100 increased.

3.3. HCB partitioning within a HACK/TX100/water system

Although the influence of TX100-HA interaction on TX100 and HA sorption to kaolin has been verified, the resultant effects on HCB partitioning in a clay/water system remain unclear. In fact, in a complicated surfactants/SOM/water/clay system, a series of sorption and complexing processes may occur and affect HCB partitioning behavior. To be more specific, these interactions include (1) the formation of DOM-HCB complex that may impede HCB sorption [10,24]; (2) the role of clay-bound SOM as a hydrophobic sorption domain for HCB [23,25,26]; (3) partitioning of HCB to TX100 micelles that can effectively reduce the potential of HCB sorption [3,27]; (4) the influence of TX100-HA interaction on TX100 and HA sorption to clay surface that may further affect the partitioning of HCB; (5) the possible sorption of HCB by the clay-bound TX100 and by the mineral [27–29].

Given the complexity of HOCs partitioning in the co-presence of TX100 and SOM, HCB sorption in SOM and TX100 individual system was investigated first. It can be found from Fig. 3a that HCB sorption correlated negatively with the amount of HA added at HA > 250 mg L^{-1}. The fraction of sorbed HCB decreased steadily from 1.0 to 0.5 as HA increased to 2500 mg L^{-1}. With the added HA increasing, the dissolved HA became increasingly abundant, therefore impeding the sorption of HCB. Nevertheless, at a low HA range of 0–150 mg L^{-1}, HCB sorption increased slightly. It is generally accepted that HA could bind HOCs through hydrophobic interactions to form HA–HOCs complexes [10,24,30], by which means the soil-bound HA sorb HOCs from solution while the dissolved HA desorb HOCs from soils. On the other hand, the formation of micelle-like structure of HA due to molecule aggregation is also proposed as the mechanism for the solubilization/enhanced desorption of HA for HOCs [9,27]. Furthermore, Fig. 3b indicates
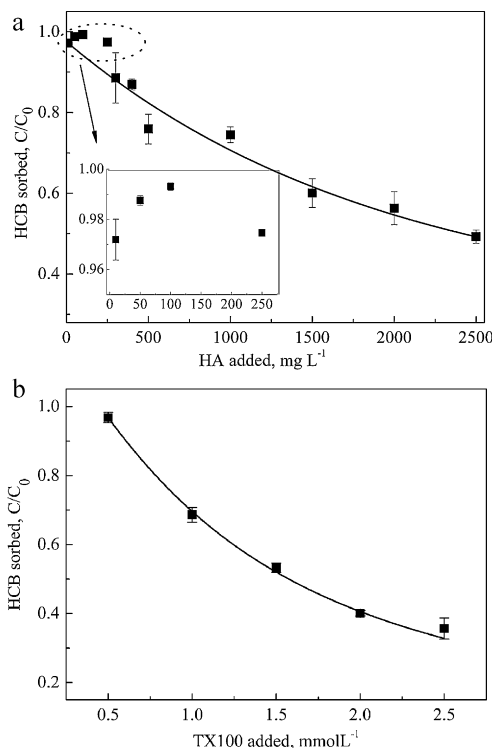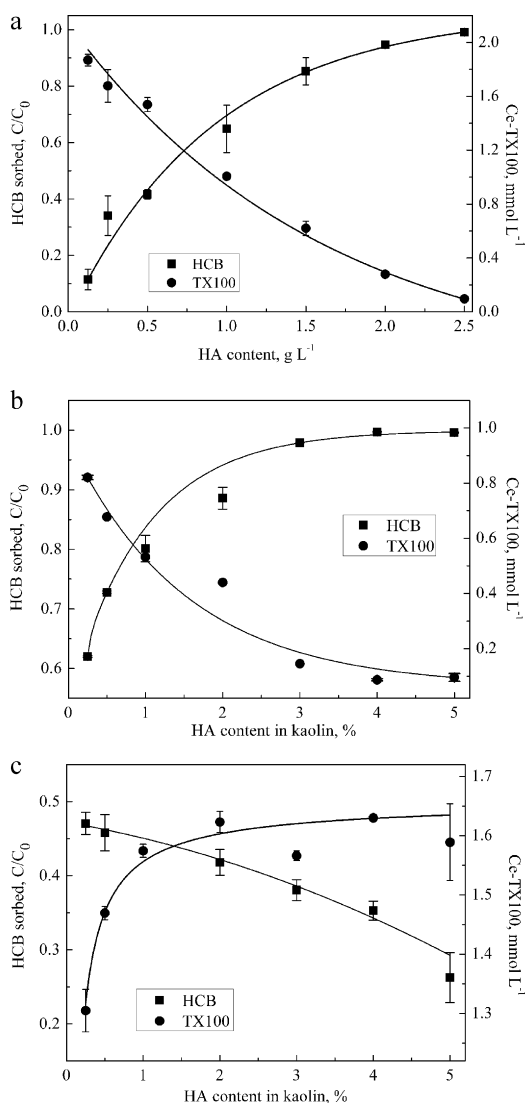
that the sorption of HCB experienced a steady decline with the increase of TX100 added (0–2 mmol L^{-1}, Fig. 3b). Particularly, when 2 mmol L^{-1} of TX100 was added, the fraction of HCB sorbed was about 0.4. It is suggested that only at total surfactant concentration above critical desorption concentration (CDC), i.e., the aqueous surfactant concentration above CMC, reliable enhancement in HCB desorption by surfactants can be obtained [3,31]. The CDC of TX100 herein can be estimated from following equation:

$$CDC = CMC + Cs_{CMC}$$

wherein Cs$_{CMC}$ is the concentration of TX100 in soil when the corresponding aqueous concentration is at the CMC, which can be calculated from Cs$_{CMC}$ = 19.1CMC/(0.085 + CMC) (Fig. 1a). By substituting the measured CMC value of TX100 of 0.1 mmol L^{-1} into above equations, the estimated CDC is 0.62 mmol L^{-1}. As a consequence, no apparent desorption of HCB was recorded at total TX100 concentration of 0.5 mmol L^{-1}, while remarkable HCB desorption was obtained at TX100 dosage above 1 mmol L^{-1}.
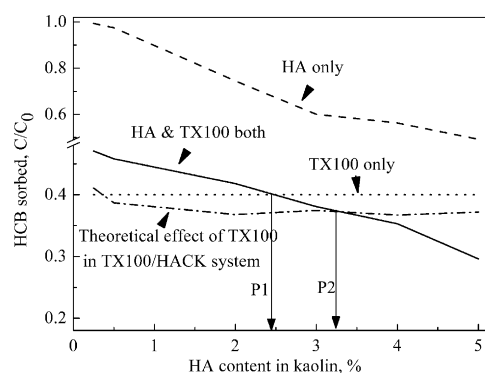
The partitioning of HCB in a HACK/TX100/water system, and the effects of clay-bound HA and dissolved HA on the sorption of HCB to HACK are illustrated in Fig. 4a–c. From Fig. 4a it is evident that the sorption of TX100 and HCB to solid HA both correlated positively with the HA content. With the HA concentration increasing from 0 to 2.5 g L^{-1}, the aqueous TX100 (initially 1 mmol L^{-1}) decreased substantially to nearly undetectable, and correspondingly, the sorption of HCB (initial aqueous concentration was 0.5 mg L^{-1}) increased steadily to 1.0. The reduced aqueous TX100 concentration was directly associated with the high affinity of HA for TX100, as the K_d values for TX100 herein were estimated as (0.6–8) × 10^3 L kg^{-1}, which are 1.8–2.9 orders of magnitude larger than that of TX100 to kaolin (10.9 L kg^{-1} at TX100 of 2 mmol L^{-1}). The reduced aqueous HCB concentration, however, was mainly relevant to the strong affinity of both HA and HA-bound TX100 [27]. The binding constant (K_b) for the HA–HCB complex was estimated as 5.5 × 10^4 L kg^{-1} by using the solubility enhancing method [24,32]

Fig. 5. Estimation of factors contributed to HCB sorption, wherein "HA only" and "TX100 only" represent HCB sorption as the inherent effect of HA (Fig. 3a) and 2 mmol L^{-1} TX100 only (Fig. 3b), respectively. "Theoretical effect of TX100 in TX100/HACK system" represents the theoretical HCB sorption by TX100 under the interference of HA coating, calculated from the aqueous TX100 content (Fig. 4c) and the inherent effect of TX100 on HCB sorption (Fig. 3b).

of HA coating amount of 0.5–5% (Fig. S2, the slope of the "SOM content" linear was less than 0.5). As a consequence, the formation of aqueous HA–HCB complex became increasingly pronounced. Furthermore, the reduced sorption of TX100 by the presence of HA may be further responsible for the decreasing sorption of HCB. As indicated in Fig. 4c, the dissolved fraction of TX100 increased from 1.3 to above 1.6 mmol L^{-1} as the amount of HA coating increased, slightly deviated from the results of Fig. 1b. A plausible explanation for this deviation was that for HACK the clay surface was preliminarily occupied by HA, and the replacement of TX100 for the bound-HA was somewhat harder than the competitive sorption with the dissolved HA (Section 3.1). Finally, the possibly synergistic effect of HA–TX100 complexes on HCB solubilization and reduced adsorption in the HACK/surfactant/water systems cannot be ruled out [13].

3.4. Contributions of SOM and TX100 to HCB sorption

Based on above results of HCB partitioning behaviors in individual systems, in this section we will further summarize and compare the individual and combined roles of HA and TX100 in HCB sorption. For this purpose, Fig. 5 and Table 1 were constructed. The dashed curve (designated as "HA only", i.e., Fig. 3a) and dotted curve (designated as "TX100 only", i.e., Fig. 3b) represent HCB sorption on clay when HA (125–2500 mg L^{-1}) and TX100 (2 mmol L^{-1}) were added individually. The solid curve (designated as "HA & TX100 both", i.e., Fig. 4c) displays HCB sorption due to the copresence of TX100 and HA. The curve of dash-dot (designated as "Theoretical effect of TX100 in TX100/HACK system") is the theoretical HCB sorption caused by 2 mmol L^{-1} TX100 in the TX100/HACK system, in which the effect of additional aqueous TX100 (resulted from HA coating, Section 3.3 and Fig. 4c) on HCB sorption was involved (see detailed deduction procedure from Notes of Table 1). It should be mentioned that a neutral pH of 7.0 was set for all above systems, thus the influence of pH could be neglected. Inspection of Fig. 5 indicates that TX100 played a dominant role in the reduction of HCB sorption. Other than increasing HCB solubility by the inherent aqueous TX100 (in HA-free system), the reduced sorption of TX100 due to the co-presence of HA may lower the sorption of HCB additionally. This additional fraction of sorbed HCB was expected to be about 0.04, as revealed by comparing the result of "TX100-observed" and "TX100-Theoretical in TX100/HACK system" (Table 1). However, the effect of HA coating on HCB partitioning was dual depending on the coating amount. Although a dramatic decline in HCB sorption was obtained as a function of increasing HA coating in the whole range, the presence of HA was found to promote the HCB sorption

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Fig. 4. Partitioning of TX100 and HCB within (a) solid HA/water, (b) HACK/water (pH 3.0) and (c) HACK/water (pH 7.0) system. Initial concentrations for HCB and TX100 were 0.5 mg L^{-1} and 2 mmol L^{-1}, respectively.

(detailed in the notification of Fig. S1 in Supplementary Materials), suggesting a rather strong interaction between HA and HCB. Furthermore, the reduced aqueous TX100 concentration as a function of solid HA could also contribute to the increased sorption of HCB considering the poor inherent solubility of HCB in water. Similar trends for TX100 and HCB sorption were also observed in the HACK/water system at pH 3 (Fig. 4b). Note that much lower aqueous TX100 (about 0.9 mmol L^{-1}) and higher HCB sorption (over 0.6) were recorded at a very low HA content of 0.25% (Fig. 4b), which can be mainly attributed to the sorption by kaolin. The important role of mineral components in the partitioning of either surfactants or HOCs especially at low organic carbon contents has been addressed by other researchers [33,34].

Fig. 4c depicts the partitioning of TX100 and HCB at pH 7.0 within the HACK/water system. Contrary to the trends at pH 3.0 (Fig. 4b), the fraction of sorbed HCB decreased from 0.47 to 0.26 with the HA coating ranging from 0.25% to 5%. The declining sorption of HCB was consistent with the aforementioned observations in the HA/kaolin system (Fig. 3a). It is noteworthy to address that although an increase in HA coating may result in a direct increment in SOM content of kaolin, the fraction of dissolved HA was apparently higher than the fraction bound to kaolin all along the range

Table 1
Contributions of TX100 and HA to HCB desorption from HACK.

HA coating (%)	Fraction of HCB desorbed in different systems, Ce/C_0				
	HA-observed[a]	TX100-observed[a]	TX100-theoretical in HACK/TX100 system[b]	HA & TX100 both-theoretical[c]	Sum-HA & TX100 individually[d]
0.5	0.03	0.59	0.61	0.53	0.61
1.0	0.24	0.59	0.63	0.54	0.83
2.0	0.26	0.59	0.63	0.58	0.84
3.0	0.40	0.59	0.63	0.62	0.99
4.0	0.44	0.59	0.63	0.65	1.03
5.0	0.50	0.59	0.63	0.74	1.10

[a] The observed fraction of HCB desorption by HA individually (results of Fig. 3a). Similar for "TX100-observed" (results of Fig. 3b).
[b] The theoretical fraction of HCB desorption as an effect of $2\,mmol\,L^{-1}$ TX100 in an TX100/HACK system, calculated by substituting the value of the aqueous TX100 (Fig. 3c) to the following equation that correlates HCB sorption to aqueous TX100 concentration:

$$F_{HCB} = \frac{0.109 + 1.08}{1 + 1.95Ce_{TX100}{}^{0.946}}$$

wherein F_{HCB} is the fraction of HCB sorbed to HACK, Ce_{TX100} is the aqueous TX100 concentration.
[c] The observed fraction of HCB desorption as the effects of both HA coating and TX100 addition.
[d] The theoretical fraction of HCB desorption by TX100 and HA, i.e., the sum of fraction of HCB desorption by HA and TX100 individually.

at lower coating amounts if taking the result of "TX100 only" (Fig. 5) as the reference. As discussed above, the competition between the aqueous and clay-bound HA determines the effect of HA coating on HCB sorption [10,23], regardless of the interference by TX100. Note that the intersection point of the "HA & TX100 both" and the "TX100 only" curve (P1 in Fig. 5) represents an equilibrium of the facilitating and impeding role of HA coating in HCB sorption. It is speculated that only at HA coating higher than 2.4%, the dissolved HA outcompeted the clay-bound HA for HCB partitioning. Excess HCB desorption from clay-bound HA could be reached due to this dissolved HA, compared to HCB desorptoion by TX100 alone. If we actually take the additional effect of sorption reduction of TX100 into account, the intersection would shift toward the higher HA coating, as depicted in Fig. 5 (P2), which means the positive effects on the reduction of HCB sorption by HA is expected at the coating amount above 3.3%.

Inspection of Fig. 5 further reveals that P1 is actually the critical point at which the combined effects of HA and TX100 on HCB sorption equals to that of TX100 alone. That implies that at HA coating higher than P1, the co-presence of TX100 and HA resulted in less HCB sorption than either HA or TX100 alone. Nevertheless, as indicated by Table 1, the combined effect on reduction of HCB sorption was less than the sum of TX100 and HA alone. The results seemingly conflict with previous observations that a synergistic effect on HOCs desorption from soil by co-addition of Tween 80 and DOM was recorded [13]. However, note that the soil texture (one loam sandy soil) and the procedures for agents adding (simultaneous addition of Tween 80 and DOM into the system) therein would probably generate less sorption of DOM as compared with the HACK in our study. Furthermore, since the fractions of HCB "desorption" were 60% and over 40% for TX100 ($2\,mmol\,L^{-1}$) and HA (at HA-coating ≥2%) individually (Table 1), no synergistic or even additive effect can be expected by the combination of TX100 and HA; while as reported by Cheng and Wong [13], even when a synergistic effect was reached, the maximal desorption ratio was as low as 16.2% and 10.9% for phenanthrene and pyrene, respectively. We presumed that similar synergistic or additive effect by the copresence of TX100 and HA can be reached if a proper TX100 and HA concentration was applied (at least, the sum of HCB desorption efficiency by TX100 and HA alone was apparently below 100%).

4. Conclusions

A deeper insight into the combined effect of surfactants, SOM, and DOM on HOC adsorption in a soil/water system is required to

better predict the efficacy of SER. Herein we investigated the partitioning of HCB in a HACK/water system in the presence of TX100. Main conclusions can be summed up as follows:

(1) Appreciable influence of TX100-HA interaction on TX100 and HA sorption to clay was observed. The addition of HA at lower and higher amount than $1500\,mg\,L^{-1}$ was found enhancing and reducing the sorption of TX100 to kaolin, respectively. Furthermore, the presence of TX100 suppressed the sorption of HA to kaolin over the entire observed concentration range of $0.5–2\,mmol\,L^{-1}$. The presented results suggest that for soils of high organic contents, the surfactant-SOM interaction may be beneficial to SER. In addition, a properly high dosage of surfactant may be more preferable to dissolve the SOM and exert such extra desorption.

(2) TX100 contributed primarily to HCB desorption in a HACK/TX100/water system. DOM also showed encouraging enhancement in HCB desorption. The coated HA, however, imposed a negative and positive influence on TX100-enhanced desorption of HCB at coating amounts below and above 2.4%, respectively. The combined effect of HA and TX100 on HCB desorption was less than the sum of TX100 and HA alone.

(3) It should be noted that HACK may or may not fully represent the whole soil in nature. However, the results we obtained are still of practical significance for SER since HA is often intimately associated with clay minerals in soil, and both HA and clay minerals are primary soil compounds that determine the sorption of surfactants and HOCs, i.e., the performance of SER.

(4) Our study suggests that for soils of high organic contents, a combined influence of SOM and surfactants on HOCs removal can be expected, which implies a higher performance of SER, or a smaller dosage of surfactant may be required. However, the critical content of SOM that differentiates the positive role of SOM from the negative one in the SER has been revealed herein, the value may vary from site to site, depending on a series of factors such as characteristics of soil, SOM, surfactants, and HOCs. Furthermore, pH as an important environmental variable may influence the amount of DOM, therefore influencing the SER process. However, for the consideration of system simplification, in present study we only chose pH 7 as a typical circumstance. As a result, further studies are still required to focus on the combined effect of surfactants and SOM on SER for real soils with different organic contents, a broader range of pH conditions and a variety of HOCs.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.08.072.

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