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# Selective sorption of PAHs from TX100 solution by resin SP850: effects of TX100 concentrations and PAHs solubility†

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Recycling of washing effluent by selective sorption using resins is a feasible method to lower the operation costs of surfactant enhanced remediation (SER). In this study, correlations capable of predicting the selective sorption removal of polycyclic aromatic hydrocarbons (PAHs) by resin SP850 from TX100 solution to recycle washing effluent in SER were developed. A negative relationship of sorption coefficients ( $\log K_f$ ) of PAHs by resin SP850 with TX100 initial concentrations ( $\log C_{0, \text{TX100}}$ ) and water solubilities ( $\log S_w$ ) of PAHs was observed, which indicated that solubility enhancement of PAHs in TX100 micelles was responsible for the decreasing of the selective sorption. Freundlich exponential coefficients ( $1/n$ ) of PAHs were relatively constant ( $0.775 \pm 0.012$ ), suggesting that the sorption of PAHs by SP850 in the presence of surfactant is a surface adsorption process. The modified selectivity parameter ( $S^*$ ), having a relationship with  $\log C_{0, \text{TX100}}$  and PAHs  $\log S_w$  as well, could be employed to evaluate the efficiency of the selective sorption process and select the optimal TX100 concentration in washing effluents. For example, at the given SP850 dose of  $1.0 \text{ g L}^{-1}$ , the optimal TX100 concentrations ( $C_{\text{optTX100}}$ ) for naphthalene, acenaphthene, phenanthrene, pyrene, anthracene and benzantracene were about 4200, 7100, 8000, 10 000, 18 000 and 19 500  $\text{mg L}^{-1}$ , respectively, having a negative relationship with their  $\log S_w$ . Moreover, the  $C_{\text{optTX100}}$  was independent of the solid-to-solution ratio of SP850 and TX100 solution containing PAHs. These correlations would be helpful for the application of SER in contaminated soils by giving a method to quantitatively predict the selective sorption behaviors of PAHs by SP850 from TX100 solution, especially for the  $C_{\text{optTX100}}$ , using the  $S_w$  of organic compounds and surfactant concentrations.

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## Introduction

Surfactant enhanced remediation (SER) has been suggested as a promising technology in removing hydrophobic organic compounds (HOCs) such as polycyclic aromatic hydrocarbons (PAHs) from contaminated soils and groundwater.<sup>1–8</sup> However, the practical implementation of SER in contaminated soils is limited due to the increased operation costs produced by the usage of large volumes of surfactant solutions during the soil washing process and the disposal of washing effluents.<sup>9–12</sup> Washing effluents containing high concentrations of

surfactants and HOCs were obtained from soil washing by separation using centrifugation or precipitation to remove soil solids.

Sorption treatment has been regarded as a promising separation and purification method.<sup>13–16</sup> Recycling of washing effluents by selectively sorption separating of HOCs from surfactant solutions and remaining surfactant in solutions is an economical and effective strategy to reduce the operation costs of SER.<sup>17–22</sup> In our previous study,<sup>23</sup> we found that resin SP850, with higher percent removal for phenanthrene from surfactant solutions and easy regeneration, was a better sorbent than activated carbon and organo-bentonite for the selective separation of phenanthrene from surfactant solutions and the recycling of washing effluents. For example, at  $5000 \text{ mg L}^{-1}$  TX100 solution, the removal percentage of phenanthrene from TX100 solution by  $1.0 \text{ g L}^{-1}$  SP850 was 82.8%, higher than that by activated carbon (65.9%) and organo-bentonite (63.3%). Moreover, a modified selectivity parameter ( $S^*$ ), having a parabolic relationship with surfactant equilibrium concentrations, was suggested to evaluate the efficiency of the selective sorption process for phenanthrene removal and to calculate the optimal surfactant washing concentration in washing effluents.<sup>23</sup>

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However, the application of  $S^*$  in predicting the selective sorption efficiency for other HOCs except for phenanthrene from surfactant solution should also be examined.

Surfactant concentrations used in SER and solubilization capabilities of surfactant for HOCs are commonly varied for HOCs and largely dependent of their water solubility ( $S_w$ ).<sup>24–27</sup> For example, the molar solubilization ratios (MSR), the number of moles of compound solubilized per number of moles of micellized surfactant, of phenanthrene, naphthalene, pyrene and fluoranthene in TX100 solution were 0.111, 0.338, 0.0352 (ref. 25) and 0.092 (ref. 28), respectively. The method to calculate the optimal surfactant washing concentration for HOCs in SER using  $S^*$  values should be established. Therefore, the role of surfactant concentrations and chemical solubility on the selective sorption of six PAHs by SP850 from TX100 solution were investigated in this study to develop the correlations of  $S^*$  with surfactant concentrations and chemical  $S_w$ . The developed correlations could be employed to quantitatively predict an optimal surfactant concentration in washing effluents for PAHs removal by selective sorption using SP850 from surfactant solutions. Six PAHs, including naphthalene, phenanthrene, pyrene, acenaphthene, anthracene and benzantracene, which span several orders of magnitude in  $S_w$  and commonly investigated in previous studies regarding SER technology<sup>4,10,25,29,30</sup> were examined here. TX100 employed here because it is a typical soil washing reagent due to its great abilities in enhancing solubility of HOCs.<sup>26,31–34</sup>

## Experimental

### Chemicals and resin

Naphthalene (>99%) was purchased from Acros Organics Co. Phenanthrene (>98%) and pyrene (>97%) were purchased from Fluka Chemistry Co. Acenaphthene (>98%), anthracene (>99.5%) and benzantracene (>98%) were purchased from Aladdin Chemistry Co. Selected properties of these PAHs are listed in Table 1. Nonionic surfactant, TX100 ( $C_{18}H_{17}C_6H_4O(OCH_2CH_2)_{9.5}H$ ), with purity of 98%, was purchased from Sigma Chemical Co. Critical micelle concentration (CMC) of TX100 was  $167 \text{ mg L}^{-1}$ .<sup>34</sup>

Resin SP850, a styrene macroporous resin, was purchased from Rohm and Haas Company (Philadelphia, PA, USA). Before usage, the resin was extracted with ethanol at a solid/solution

ratio of 1 g/5 mL for three times to remove the possible impurities, then washed by deionized water and dried in a vacuum oven at  $50^\circ\text{C}$ . The Brunauer–Emmett–Teller (BET) surface area and total pore volume of SP850 obtained from  $N_2$  adsorption–desorption isotherms were  $953 \text{ m}^2 \text{ g}^{-1}$  and  $1.65 \text{ cm}^3 \text{ g}^{-1}$ , respectively.

### Sorption experiments

Isotherms of selected PAHs by SP850 from TX100 solution were obtained through performing a batch equilibration technique at  $25 \pm 1^\circ\text{C}$ , as described in our previous paper.<sup>23</sup> SP850 was mixed with 20 mL of aqueous solutions containing TX100 and individual PAHs. Solid-to-solution ratios ( $m : v$ ) of SP850 and solutions were controlled to achieve more than 20% removal of PAHs and TX100 by SP850. PAHs was dissolved in methanol as stock solution, and then diluted to different initial concentrations (ranged from  $0.1 \text{ mg L}^{-1}$  to  $100 \text{ mg L}^{-1}$ ) with the TX100 solution to simulate the soil washing effluent. The used TX100 initial concentrations in this study were 1500, 2000, 3000, 5000, 8000 and  $10\,000 \text{ mg L}^{-1}$ , respectively, all greater than 2CMC.<sup>1,23</sup> The volume fraction of PAHs methanol in TX100 solution was controlled less than 2% to avoid the cosolvent effects. The mixtures in the vials were shaken at 150 rpm for 2 hours to reach sorption equilibrium. Then, SP850 was separated from aqueous solution by standing vials for 20 min. Equilibrium concentrations of TX100 and PAHs in the aqueous phase were determined by the reverse phase HPLC (Shimadzu, LC-20A series, XDB-C18,  $\phi 4.6 \times 150 \text{ mm}$ ) with a UV-spectro at a flow rate of  $1 \text{ mL min}^{-1}$  using mobile phase containing 90% methanol and 10% water. The UV wavelength of 224 nm is used for TX100 analysis. The UV wavelengths ( $\lambda_{\text{max}}$ ) for naphthalene, acenaphthene, phenanthrene, pyrene, anthracene and benzantracene are listed in Table 1. Experiments uncertainties evaluated using PAHs and TX100 solutions without resin were less than 4% of the initial PAHs and TX100 concentrations. Therefore, the sorbed amounts of PAHs and TX100 by SP850 were calculated directly by the mass difference in initial and equilibrium solutions.

### Isotherm fitting and data analysis

Freundlich model (eqn (1)), a commonly empirical formula used to fit the isotherms of organic compounds by adsorbents in the presence of surfactant,<sup>20,36,37</sup> was employed in this study to fit the isotherms of PAHs from TX100 solution by SP850.

$$q_e = K_f C_e^{1/n} \quad (1)$$

where  $q_e$  ( $\text{mg g}^{-1}$ ) is the equilibrium adsorbed concentration;  $C_e$  ( $\text{mg L}^{-1}$ ) is the equilibrium aqueous concentration;  $K_f$  [ $(\text{mg g}^{-1})/(\text{mg L}^{-1})^{1/n}$ ] is Freundlich affinity coefficient;  $1/n$  is the Freundlich exponential coefficient.

The feasibility and efficiency of the selective sorption process for HOCs removal from surfactant solutions were evaluated by the modified selectivity parameter ( $S^*$ , in eqn (2))

$$S^* = (\log K_f)/(K_{f,\text{TX100}}) \quad (2)$$

Table 1 Selected properties of PAHs<sup>a</sup>

Compounds	Formula	MW	$S_w$ ( $\text{mg L}^{-1}$ )	$\log K_{ow}$ ( $25^\circ\text{C}$ )	$\lambda_{\text{max}}$
Naphthalene	$C_{10}H_8$	128	31.7	3.30	219
Acenaphthene	$C_{12}H_{10}$	154	3.8	3.92	226
Phenanthrene	$C_{14}H_{10}$	178	1.29	4.46	250
Pyrene	$C_{16}H_{10}$	202	0.135	4.88	334
Anthracene	$C_{14}H_{10}$	178	0.045	4.45	254
Benzantracene	$C_{18}H_{12}$	228	0.011	5.90	277

<sup>a</sup>  $S_w$  and  $\log K_{ow}$  reported by Yaws.<sup>35</sup>



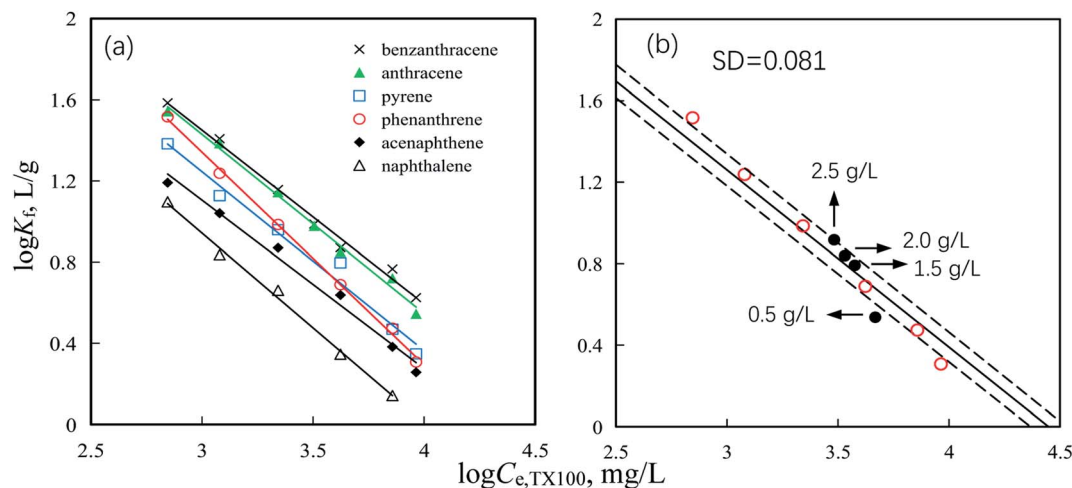


Fig. 1 Correlations of PAHs sorption coefficient ( $\log K_f$ ) by SP850 with TX100 equilibrium concentrations ( $\log C_{e,TX100}$ ) (a) and that of phenanthrene at various SP850 dose (b). Solid lines are the fitted lines. Dashed lines indicate the SD values from the fit line. Data of phenanthrene at 0.5, 1.5, 2.0 and 2.5 g L<sup>-1</sup> SP850 were from ref. 23.

where  $K_f$  [(mg g<sup>-1</sup>)/(mg L<sup>-1</sup>)<sup>1/n</sup>] is the sorption coefficient of PAHs by resin from surfactant solutions, which obtained from the Freundlich model fitted isotherms of PAHs by SP850 from TX100 solution.  $K_{f,TX100}$  (L g<sup>-1</sup>) is the sorption coefficient of TX100 by resin. In our previous study,<sup>23</sup> the distribution coefficient ( $K_d$ ) was used to calculate the  $S^*$  values.  $K_f$  and  $K_d$  are both the ratio of sorption amounts of PAHs on SP850 to equilibrium concentrations of PAHs in surfactant solutions. However,  $K_d$  values would change with the variation of PAHs concentrations when the isotherms of PAHs were nonlinear. While the  $K_f$  values would keep constant and were independent of the concentrations of PAHs, *i.e.*,  $K_f$  values could normalize the sorption ratio per unit mass when the equilibrium concentrations of solutions reached the unit value. Therefore,  $K_f$  had a wider application scope than  $K_d$  and was used in this

study to calculate the  $S^*$  values. Higher  $S^*$  value indicates more feasibility and better efficiency for the removing HOCs and the recovering surfactant solution by selection sorption. Standard deviation (SD) between experimental data and the correlations was calculated using eqn (3),

$$SD = \sqrt{\frac{\sum (D_{exp} - D_{cal})^2}{N - 1}} \quad (3)$$

where  $D_{exp}$  and  $D_{cal}$  are data determined from experiment and calculation, respectively;  $N$  is the number of data points.

## Results and discussion

Isotherms of PAHs, including naphthalene, acenaphthene, phenanthrene, pyrene, anthracene and benzantracene, by SP850 from TX100 solutions were nonlinear and fitted well by Freundlich model (Fig. S1 and Table S1†), as indicated by correlation coefficient values ( $R^2$ ) close to 1 and the significance of  $F$  test ( $P < 0.001$ ) (Table S1†). The fitted parameters (*i.e.*,  $K_f$  and  $1/n$ ) of Freundlich model for isotherms of PAHs by SP850 from TX100 solution are listed in Table S1.† Negative relationships of PAHs sorption coefficients ( $\log K_f$ ) by SP850 with TX100 equilibrium concentrations ( $\log C_{e,TX100}$ ) were observed (Fig. 1a and Table S2†), indicating that higher TX100 equilibrium concentrations will decrease the sorption of PAHs by SP850. These negative relationships should be attributed to the solubility enhancement of PAHs into TX100 micelles in solution, as has been suggested widely in the previous studies.<sup>25,29,38–40</sup> For example, the apparent solute soil-water distribution coefficients decreased with increasing  $C_{e,TX100}$  at  $C_{e,TX100}$  greater than 2CMC,<sup>10,39</sup> which was consistent with the above observation. At  $C_{e,TX100} > 2CMC$ , sorption of TX100 on SP850 reached a saturation value (788 mg g<sup>-1</sup>).<sup>23</sup> Therefore, no more PAHs can be competitively by the adsorbed TX100 micelles. However, more TX100 micelles formed in water once more TX100 were added,

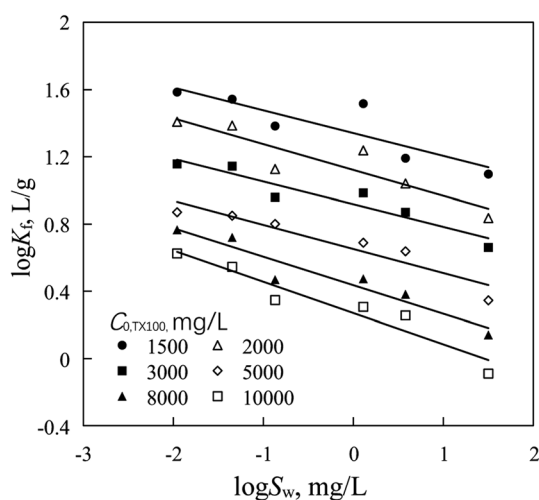


Fig. 2 Correlations of PAHs sorption coefficient ( $\log K_f$ ) with water solubility ( $\log S_w$ ) of PAHs at given TX100 initial concentrations ( $C_{0,TX100}$ ).



which can as an effective partitioning medium to decrease PAHs sorption by solubility enhancement. These negative relationships were independent of the solid-to-solution ratio of resin SP850 and TX100 solution containing PAHs. For example, at given SP850 doses of 0.5, 1.5, 2.0 and 2.5 g L<sup>-1</sup>, the phenanthrene sorption coefficients by SP850 from TX100 solution reported in our previous study,<sup>23</sup> were followed into the observed negatively relationship (Fig. 1b).

At a given TX100 initial concentration, PAHs sorption coefficient (log  $K_f$ ) was also negatively correlated with PAHs solubility (eqn (4), Fig. 2 and Table S3†).

$$\log K_f = \alpha \times \log S_w + \beta \quad (4)$$

where  $\alpha$  and  $\beta$  are the slope and intercept, respectively. The observed negative relationship between log  $K_f$  and log  $S_w$  was in agreement with the previous observations, for example, the sorption coefficients of PAHs by soils from TX100 solution at a given surfactant concentration correlated inversely with  $S_w$  of organic compounds<sup>41</sup> and decreased with the increasing  $S_w$  of pesticides.<sup>42</sup> Organic compounds with larger  $S_w$  have higher molar solubilization ratio (MSR) in TX100 solution<sup>3,25,43</sup> to partition into the surfactant micelles in solution, and thus have lower sorption coefficients by SP850. For example, the sorption coefficient of naphthalene with water solubilities of 31.7 mg L<sup>-1</sup> by SP850 at TX100 solution with initial concentration of 5000 mg L<sup>-1</sup> is 2.22 L g<sup>-1</sup>, lower than that of pyrene (6.26 L g<sup>-1</sup>) having lower water solubility of 0.135 mg L<sup>-1</sup> (Table S1†). The  $\alpha$  values in eqn (4) obtained by plotting log  $K_f$  against log  $S_w$  are almost constant (Table S3†) with a mean value of  $-0.154 \pm 0.030$  (Fig. 3a) and independent on the TX100 concentrations. The absolute values of  $\alpha$  for resin SP850 are smaller than that for Ca-montmorillonite ( $0.277 \pm 0.060$ ),<sup>42</sup> implying that the negative influence of  $S_w$  on PAHs sorption (*i.e.*, solubility enhancement effect) was less significant for SP850 than that by Ca-montmorillonite. Intercepts of eqn (4) ( $\beta$ , L g<sup>-1</sup>) were the

sorption coefficients of PAHs by SP850 (log  $K_f$ ) from TX100 with chemical solubilities closing to 1. A negatively relationship between  $\beta$  (data listed in Table S3†) and log  $C_{e,TX100}$  was observed (Fig. 3b and eqn (5)), further indicated the accuracy of the negative relationships of log  $K_f$  and log  $C_{e,TX100}$  (Fig. 1a and Table S2†). In our previous study,<sup>23</sup> a positively linear relationship between log  $C_{e,TX100}$  and TX100 initial concentrations (log  $C_{0,TX100}$ ) was observed at  $C_{e,TX100}$  higher than 2CMC (eqn (6)), where the sorption of TX100 on SP850 reached a saturated value of 788 mg g<sup>-1</sup>. Combining eqn (4)–(6), therefore, the relationship of PAHs sorption coefficient (log  $K_f$ ) by SP850 with TX100 initial concentrations (log  $C_{0,TX100}$ ) and PAHs solubilities (log  $S_w$ ) could be established (eqn (7)), which could be used to quantitatively estimate the sorption of organic compounds by SP850 from TX100 solution. The smaller absolute coefficient of log  $S_w$  (0.145) than that of log  $C_{0,TX100}$  (1.20) in eqn (7), implying that the negative effect of  $S_w$  on  $K_f$  is much weaker than that of  $C_{0,TX100}$ . The calculated log  $K_f$  (log  $K_{f,cal}$ ) values of 6 PAHs using eqn (7), are well agreed with the experimental log  $K_f$  values (log  $K_{f,exp}$ ) (Fig. S2†), which derived from Freundlich model fitted isotherms of PAHs by SP850 from TX100 solution.

$$\beta = -0.927(\pm 0.032)\log C_{e,TX100} + 3.99(\pm 0.11), \\ R^2 = 0.995, F = 822, P < 0.001, N = 6 \quad (5)$$

$$\log C_{e,TX100} = 1.33(\pm 0.06)\log C_{0,TX100} - 1.33(\pm 0.20), \\ R^2 = 0.992, F = 588, P < 0.001, N = 7 \quad (6)$$

$$\log K_f = -1.20(\pm 0.04)\log C_{0,TX100} - 0.145(\pm 0.011)\log S_w \\ + 5.12(\pm 0.16), R^2 = 0.964, F = 450, \\ P < 0.001, N = 37 \quad (7)$$

Freundlich model fitted  $1/n$  is a parameter to describe the non-linearity of isotherms.<sup>20,36</sup> For SP850,  $1/n$  values of 6 PAHs by SP850 at given TX100 initial concentrations were relatively constant, with a mean value of  $0.775 \pm 0.012$  (Fig. S3†), which

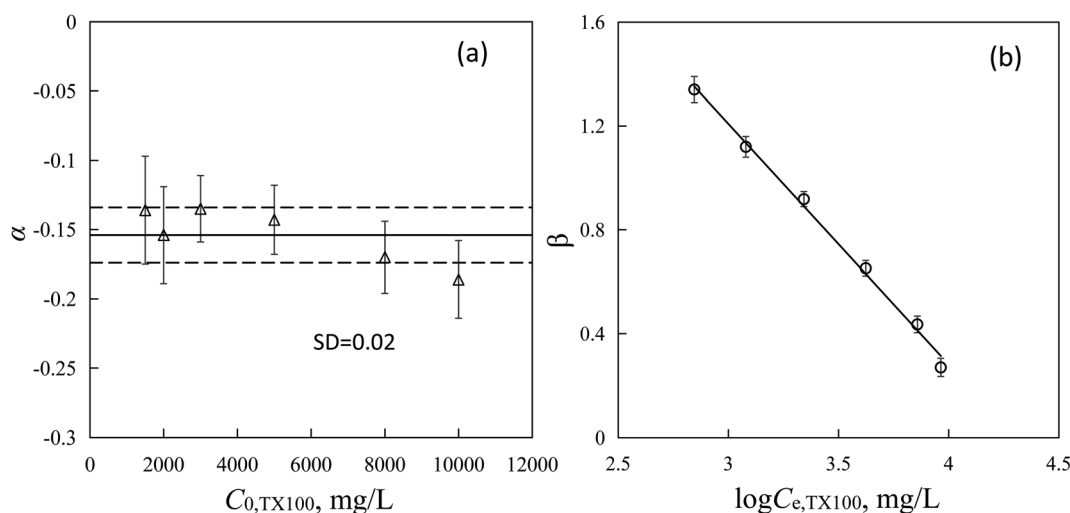


Fig. 3 Values of  $\alpha$  with TX100 initial concentrations (a) and linear relationship of  $\beta$  values with TX100 equilibrium concentrations ( $C_{e,TX100}$ ) (b). Dashed lines indicate the SD value from the reference line.





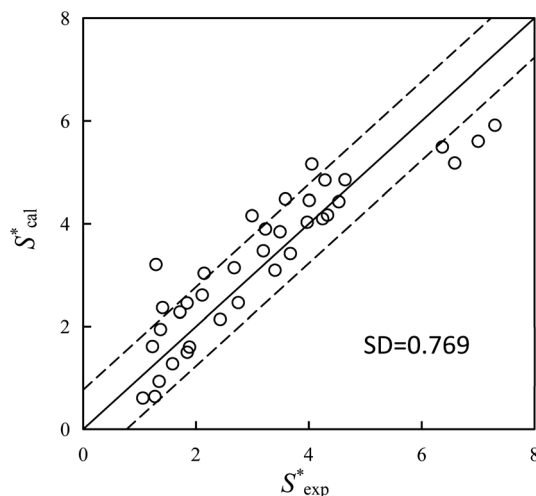


Fig. 4 Calculated  $S^*$  values ( $S^*_{\text{cal}}$ ) using eqn (9) versus the experimental  $S^*$  values ( $S^*_{\text{exp}}$ ). Solid lines is the reference line,  $y = x$ , indicating that the  $S^*_{\text{cal}}$  values equal to the  $S^*_{\text{exp}}$  values. Dashed lines indicate the SD values from the reference lines.

was smaller than that of organo-layered double hydroxide (organo-LDH with  $1/n \approx 1.0$ )<sup>20</sup> and organo-bentonite with  $1/n \approx 1.0$ .<sup>10</sup> This indicating that the sorption of PAHs by SP850 in the presence of surfactant is a surface adsorption process, while that by the organo-LDH and organo-bentonite is a partition-dominated process.

The modified selectivity parameter ( $S^*$ ), *i.e.*, the ratio of  $\log K_f$  to  $K_{f,\text{TX100}}$ , was suggested to evaluate the efficiency of the selective sorption process and optimize the surfactant concentration for SER.<sup>23</sup>  $K_{f,\text{TX100}}$ , the ratio of the adsorbed amount of TX100 on SP850 to  $C_{e,\text{TX100}}$ , has a negative relationship with  $C_{e,\text{TX100}}$  at  $C_{e,\text{surf}} > 2\text{CMC}$  (eqn (8)), where the sorption amount of TX100 reached the saturation.<sup>23</sup> According to eqn (2) and (6)–(8),  $S^*$  was related to  $\log C_{0,\text{TX100}}$  and  $\log S_w$  of PAHs. Moreover,

the concentrations of surfactants and the properties of PAHs could both affect the selective sorption of PAHs by adsorbents from surfactant solutions,<sup>9–11</sup> *i.e.*,  $\log C_{0,\text{TX100}}$  and  $\log S_w$  of PAHs are the predominant factors accounting for the selective sorption of PAHs by SP850 from TX100 solution. Therefore, multiple linear regression can be conducted between  $S^*$  and these two parameters to establish a novel relationship of  $S^*$  with  $\log C_{0,\text{TX100}}$  and  $\log S_w$  of PAHs (eqn (9)). The calculated  $S^*$  values ( $S^*_{\text{cal}}$ ) using eqn (9) are in agreement well with the experimental  $S^*$  values ( $S^*_{\text{exp}}$ ) (Fig. 4), suggesting the feasibility of eqn (9) for  $S^*$  predicting. Compared to the relationship of  $S^*$  with  $C_{e,\text{TX100}}$  observed in the previous study,<sup>23</sup> by replacing  $C_{e,\text{TX100}}$  with  $C_{0,\text{TX100}}$  and adding a new parameter,  $\log S_w$ , this novel relationship is more sufficient and convenient to quantitative predict the selective sorption behaviors of PAHs by resin SP850 from TX100 solution and guide the application of SER in contaminated soil.

By selective sorption removal of PAHs from washing effluents using resin SP850, washing effluents containing surfactants can be reused to wash contaminated soil to lower the operation costs of SER. Therefore, for soil washing, the used surfactant concentrations in SER should be high enough to form large quantitative micelles for solubility enhancement of HOCs and decrease the sorption loss of surfactant in soil.<sup>1,34,41</sup> However, the higher surfactant concentrations would lead to higher spend and lower removal percentages of HOCs by adsorbents.<sup>10,41,42</sup> Thus, selecting a suitable surfactant concentration is important for the application of SER technology. To select the optimal TX100 concentrations ( $C_{\text{optTX100}}$ ) for PAHs in SER, the relationships between  $S^*$  and  $C_{e,\text{TX100}}$ , observed for phenanthrene,<sup>23</sup> were also observed for other PAHs (Fig. 5a). Values of  $S^*$  for PAHs increased firstly, and then decreased with increasing  $C_{e,\text{TX100}}$  (Fig. 5a). Solid lines represent  $S^*$  values fitted by the parabolic equation, *i.e.*,  $S^* = AC_{e,\text{TX100}}^2 + BC_{e,\text{TX100}}$ , established in our previous study,<sup>23</sup> can well describe the increasing and the followed decreasing of  $S^*$  with increasing

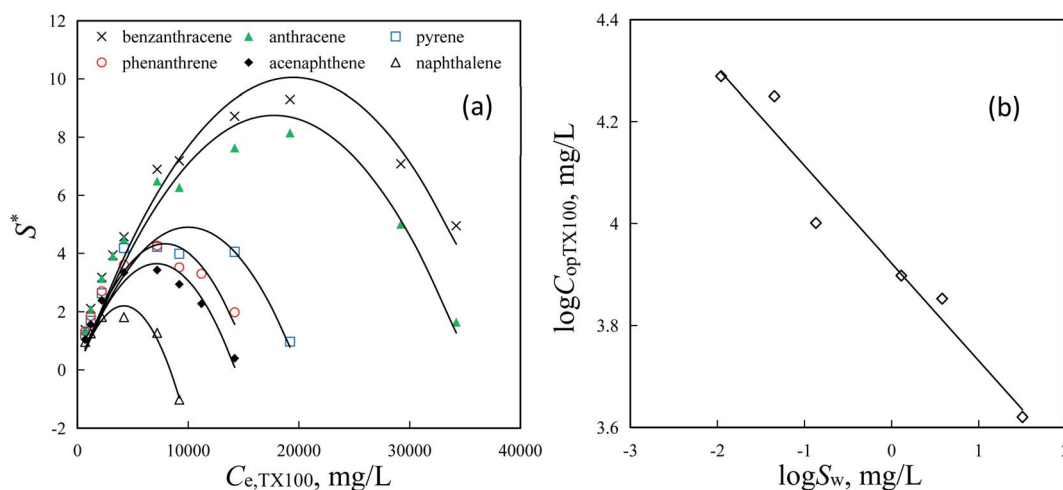


Fig. 5 Correlations between the modified selectivity parameters ( $S^*$ ) of PAHs by SP850 ( $1.0 \text{ g L}^{-1}$ ) and TX100 equilibrium concentrations ( $C_{e,\text{TX100}}$ ) (a) and the correlation of the optimal TX100 washing concentrations ( $\log C_{\text{optTX100}}$ ) with water solubility ( $\log S_w$ ) of PAHs (b). Solid lines in plots (a) and (b) are fitted by the Parabolic equation and linear equation, respectively.



$C_{e, \text{TX100}}$  (Fig. 5a and Table S4†).  $A$  and  $B$  are the coefficients of the quadratic and primary terms of the equation, respectively. For the parabolic equation, there was a maximum  $S^*$  value, which could be obtained at  $C_{e, \text{TX100}} = -B/(2A)$ , implying that  $C_{e, \text{TX100}} = -B/(2A)$  could be employed to calculate the  $C_{\text{optTX100}}$  in washing effluents for the application of SER. For example, at the given SP850 dose of  $1.0 \text{ g L}^{-1}$ , the  $C_{\text{optTX100}}$  for naphthalene, acenaphthene, phenanthrene, pyrene, anthracene and benzantracene were about 4200, 7100, 8000, 10 000, 18 000 and 19 500  $\text{mg L}^{-1}$ , respectively (Fig. 5a and Table S4†). Moreover, a negative relationship of  $\log C_{\text{optTX100}}$  with  $\log S_w$  of PAHs was observed (Fig. 5b and eqn (10)), which could be also attributed to the higher MSR of PAHs with larger  $S_w$  in TX100 solution.<sup>25,43</sup> With eqn (10), one can directly calculate the optimal TX100 concentrations in washing effluents from the  $S_w$  of organic compounds. In addition, the optimal TX100 concentrations were independent of the solid-to-solution ratio of resin SP850 and TX100 solution containing PAHs. For example, at given SP850 doses of 0.5, 1.0, 1.5 and  $2.0 \text{ g L}^{-1}$ , the similar parabolic relationships of  $S^*$  for phenanthrene by SP850 with  $C_{e, \text{TX100}}$  were obtained (Fig. S4† and eqn (11)), suggesting that the relationship of  $S^*$  with  $C_{e, \text{TX100}}$  was irrelevant to the SP850 dose. Therefore, at various SP850 doses, the optimal TX100 concentrations for the selective removal of phenanthrene by SP850 were all  $7767 \text{ mg L}^{-1}$  (Fig. S4†). The negative relationships of  $\log K_f \sim C_{e, \text{TX100}}$  and  $K_{f, \text{TX100}} \sim C_{e, \text{TX100}}$  were both independent of the solid-to-solution ratio of resin SP850 and TX100 solution containing PAHs at  $C_{e, \text{surf}} > 2\text{CMC}$  (Fig. 1b and eqn (8)) which could result in this phenomenon.

$$K_{f, \text{TX100}} = 788(\pm 7) \times C_{e, \text{TX100}}^{-1.00(\pm 0.00)}, \\ R^2 = 0.999, F = 2.42 \times 10^6, P < 0.001, N = 8 \quad (8)$$

$$S^* = -1.49(\pm 1.98)(\log C_{0, \text{TX100}})^2 \\ + 15.0(\pm 14.2)\log C_{0, \text{TX100}} - 0.693(\pm 0.112)\log S_w \\ - 31.6(\pm 25.4), R^2 = 0.805, F = 70.1, \\ P < 0.001, N = 37 \quad (9)$$

$$\log C_{\text{optTX100}} = -0.182(\pm 0.029)\log S_w + 3.94(\pm 0.04), \\ R^2 = 0.908, F = 39.3, P = 0.003, N = 6 \quad (10)$$

$$S^* = -4.59(\pm 0.21) \times 10^{-8} C_{e, \text{TX100}}^2 + 7.13(\pm 0.32) \times 10^{-4} \\ C_{e, \text{TX100}} + 1.22(\pm 0.10), R^2 = 0.948, F = 2.69 \times 10^3, \\ P < 0.001, N = 28 \quad (11)$$

## Conclusions

Effects of TX100 concentrations and PAHs solubilities on the selective sorption of PAHs by resin SP850 from TX100 solution were investigated in this study. A negative relationship of sorption coefficients ( $\log K_f$ ) of PAHs, including naphthalene, acenaphthene, phenanthrene, pyrene, anthracene and benzantracene, by resin SP850 with TX100 initial concentrations ( $\log C_{0, \text{TX100}}$ ) and water solubilities ( $\log S_w$ ) of PAHs was developed, which could be attributed to the solubility enhancement of PAHs in TX100 micelles. The modified selectivity parameter

( $S^*$ ), having a relationship with  $\log C_{0, \text{TX100}}$  and  $\log S_w$  of PAHs as well. Compared to the relationship of  $S^*$  with just TX100 equilibrium concentrations ( $C_{e, \text{TX100}}$ ) observed in the previous study,<sup>23</sup> by replacing  $C_{e, \text{TX100}}$  with  $C_{0, \text{TX100}}$  and adding a new parameter,  $\log S_w$ , this novel relationship is more sufficient and convenient to quantitative predict the selective removal of PAHs to recycle washing effluent in SER and gives new insights into the  $S^*$  values. Moreover,  $S^*$  values, having a parabolic equation with  $C_{e, \text{TX100}}$ , can be employed to evaluate the optimal TX100 concentration ( $\log C_{\text{optTX100}}$ ) in washing effluents for PAHs in SER. For example, at the given SP850 dose of  $1.0 \text{ g L}^{-1}$ , the  $C_{\text{optTX100}}$  for naphthalene, acenaphthene, phenanthrene, pyrene, anthracene and benzantracene were about 4200, 7100, 8000, 10 000, 18 000 and 19 500  $\text{mg L}^{-1}$ , respectively. The optimal TX100 concentrations for the selective removal of PAHs by SP850 had a negative relationship with  $\log S_w$  of PAHs and were independent of the solid-to-solution ratio of SP850 and TX100 solution containing PAHs. These established correlations can be employed to quantitatively estimate the selective sorption behaviors of PAHs by SP850 from TX100 solution, especially for the  $C_{\text{optTX100}}$ , using the  $\log S_w$  of organic compounds and TX100 concentrations for recycling TX100 solution in SER. In addition, more experiments such as selective sorption of HOCs from washing effluents containing mixture surfactants by resins are in urgent needed to be established for more feasible applications of resins and the modified selectivity parameter.

## Author contributions

Yaxiong Zeng: methodology, investigation, formal analysis, writing – original draft. Ming Zhang: writing – review & editing. Daohui Lin: conceptualization. Kun Yang: conceptualization, supervision, writing – review & editing, funding acquisition.

## Conflicts of interest

There are no conflicts to declare.

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