Selective adsorption of PHC and regeneration of washing effluents by modified diatomite
Zhuoqi Xu, Gengbo Ren, Yanying Zhu, Xiaodong Ma, Hongrui Li, Wangqing Zhang, Anyong Mu, Qingbin Zeng and Aiqun He

ABSTRACT
Selective removal of petroleum hydrocarbons (PHCs) from soil washing effluents is the key to the surfactant-enhanced soil washing technology. In this study, the diatomite was modified by nonionic surfactant TX-100 and applied in the selective adsorption of PHCs in the soil washing effluents. The modified diatomites were characterized by scanning electron microscopy, Fourier transform infrared spectroscopy, X-ray diffraction, N₂ adsorption/desorption and X-ray photoelectron spectroscopy respectively. The adsorption process followed the pseudo-second-order model and the adsorption isotherms indicated that the interaction between PHCs and modified diatomite was monolayer adsorption. The important operating factors such as TX-100 dosage, adsorbent dosage, time and temperature were optimized. With the participation of the low-cost adsorbent TX3-Db with high adsorption capacity, the recovery efficiency of the washing effluents was still up to 78.9% after three cycles. A selective adsorption mechanism, based on steric hindrance and electrostatic repulsion, was proposed to explain the removal of PHCs from washing effluents.

Key words | modified diatomite, nonionic surfactant, petroleum hydrocarbons, selective adsorption, washing effluents regeneration

HIGHLIGHTS
• Cheap and renewable TX3-Db was prepared and used to selectively adsorb petroleum hydrocarbons (PHCs).
• Removal of PHCs and regeneration of washing effluents can be simultaneously achieved.
• Selective adsorbents and regenerated washing effluents can be recycled.
• Selective adsorption mechanism depends on the adsorbent's hydrophobic and negative structure.

INTRODUCTION

Soil heavily contaminated by petroleum hydrocarbons (PHCs) is a serious world-wide environmental problem that has been attracting wide attention over the past decades (Vidonish et al. 2018). Among various remediation technologies, anionic–nonionic mixed surfactant-enhanced washing has been regarded as a promising remediation technology due to its high washing efficiency, which comes from the solubilization of hydrophobic organic pollutants by the formed mixed micelle (Befkadu & Chen 2018). The major challenge of this technology, however, is how to achieve the regeneration of its washing effluents. The remediation cost of surfactant-enhanced washing technology will be greatly increased if the surfactant in the washing effluents cannot be reused. In addition, the residual PHCs may cause new risk of secondary environmental pollution (Gomez et al. 2010).

The key to recovering the function of washing effluents is to remove the PHCs in effluents, simultaneously retaining
the surfactants. Adsorption technology has been widely applied in the removal of organic pollutants from the water environment because of its simple operation and high efficiency (Alshammari et al. 2020). In this regard, carbon materials with very high specific surface area are important adsorbents that are widely applied in adsorption of hydrophobic pollutants from wastewater. Dispersed oil could be effectively removed from contaminated water by activated charcoal adsorbent based on the hydrophobic interactions and π–π interaction (Ji et al. 2019). A petroleum coke-based porous carbon was rather effective in the adsorption of mixed polycyclic aromatic hydrocarbons by the combined action of the H-bonding formation, the π–π interaction and the electron donor–acceptor interaction (Yuan et al. 2010). Pretty high adsorption efficiency of PHC from the contaminated ground water could be obtained using powder activated carbon (Wang et al. 2017). Unfortunately, these reported adsorbents have the following shortcomings: (i) the anaerobic calcination at high temperature and chemical activation in the preparation process would cause high production costs; (ii) lack of selective adsorption for the hydrophobic pollutants. Therefore, there is an urgent need to develop low-cost alternative materials to selectively adsorb PHCs from washing effluents.

Diatomite-based adsorbent has received extensive attention during its low cost, it is derived from an abundant resource and its easy surface modification. Raw diatomite, as an efficient adsorbent, has been used to remove organic pollutants from wastewater (Khraisheh et al. 2005). Further researches showed the adsorption efficiency of diatomite could be further improved based on the modification of the surface structure and charge (Nosrati et al. 2017). However, the related works are not profound, especially in the selective adsorption of the hydrophobic organic pollutants from wastewater (Alshammari et al. 2020). There is also lack of systematic examination on the structure–reactivity correlations in the adsorption process based on modified diatomite adsorbent (Zhang et al. 2018).

In this work, a novel hydrophobic diatomite with negative surface charge was designed based on the surfactant surface modification with nonionic surfactant TX-100 and used in the selective adsorption of PHCs. The surface morphology and characterization were examined by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), N2 adsorption/desorption and X-ray photoelectron spectroscopy (XPS). Adsorption capacity, kinetics and isotherms were systematically investigated. The operating factors modifier dosage, adsorbent dose, time and temperature were systematically and optimized. The recyclability of washing effluents and modified diatomite adsorbents was evaluated. A selective adsorption mechanism was proposed based on analysis of the structure–activity relationship.

MATERIALS AND METHODS

Materials

Natural diatomite (D) and TX-100 (the purity >99%) were supplied by Tianjin Kemiu Chemical Reagent Co., Ltd, China. Sodium silicate and sodium hydroxide were purchased from Jiangtian Chemical Industry Technology Co., Ltd, China. Sulfuric acid and deionized water were obtained from Huadong Chemical Reagent Co., Ltd, China.

Preparation of the modified diatomite and soil washing effluent

Natural diatomite was washed with deionized water and dried at 100 °C in the oven. Five grams of dried D was added to 80.0 mL of 0.6 M NaOH solution and stirred for 1 h at room temperature. The above treated D was washed with deionized water, and then dried at 100 °C. This sample was denoted as the alkali-pretreated diatomite (Db). The Db was added into 80.0 mL nonionic surfactant (TX-100) solution under stirring to obtain the TX-100-modified diatomite (TX3-Db), which was then treated in an ultrasonic bath for 10 min. Finally, the above sample was washed with deionized water and dried at 100 °C.

Petroleum-contaminated soil was collected from a sewage plant of Dongying city, China. The concentration of PHCs in the contaminated soil was 230.0 g/kg, which was measured by the gravimetric method. The collected soil was crushed and screened through 0.1 mm sieve. Three grams of soil and 100.0 mL washing solution, which consisted of 0.24 g anionic surfactant (linear alkylbenzene sulfonate), 0.06 g nonionic surfactant (TX-100) and 0.5 g sodium silicate, were mixed and treated in an ultrasonic bath for 15 min, and then put into a water bath at 75 °C for 1 h. The soil suspensions were centrifuged at 3,000 rpm for 30 min to obtain the soil washing effluents.

Adsorbent characterizations

The surface morphology of adsorbents was evaluated by SEM (Shimadzu SS-550). The XRD was carried out to identify the crystal phases of adsorbents using a Rigaku
D/Max-2500 powder diffractometer in the range of 5–80° at a scan speed of 6°/min. FTIR spectra of the adsorbents were obtained using a Bruker Tensor 27 spectrometer in the range of 400–4,000 cm⁻¹. Nitrogen adsorption/desorption isotherms of adsorbents were measured at 77 K in a Quantachrome NOVA 2000e type of sorption analyzer for 4 h. The Brunauer–Emmett–Teller (BET) surface area was measured according to the nitrogen adsorption/desorption data. BJH (Barrett–Joyner–Halenda) method was used to determine the pore size distribution. XPS was performed using a spectrometer (Thermo Fisher Scientific ESCALAB 250Xi) with monochromated Al Kα radiation.

**The regeneration of washing effluents**

Adsorbents (0.5 g) and 100.0 mL washing effluents were mixed and stirred at room temperature for 30 min. Mixed suspensions were then centrifuged at 3,000 rpm for 10 min to obtain the regenerated washing effluents. Regenerated washing effluents were utilized to wash the contaminated soil. The regeneration efficiency of washing effluents was evaluated with the indicator of washing efficiency (WE) as follows:

\[
WE = \frac{C_0 - C_t}{C_0} \times 100\%  \quad (1)
\]

where \(C_0\) and \(C_t\) are the concentration of PHCs in unwashed contaminated soil and washed soil using regenerated washing effluents, respectively.

In addition, the recyclability of washing effluent and adsorbent was further evaluated and reflected by recovery efficiency (RE) as in the following Equations (2) and (3),

\[
RE_{\text{ef}} = \frac{WE_{\text{ef}}}{WE_0} \times 100\%  \quad (2)
\]

\[
RE_a = \frac{WE_2}{WE_1} \times 100\%  \quad (3)
\]

where \(RE_{\text{ef}}\) is the recovery efficiency of washing effluent; \(WE_0\) and \(WE_2\) are the washing efficiency of the original and regenerated washing effluents, respectively.

\[
RE_a = \frac{WE_2}{WE_1} \times 100\%  \quad (3)
\]

where \(RE_a\) is the recovery efficiency of TX3-Db adsorbent; \(WE_1\) and \(WE_2\) are the washing efficiency of the regenerated washing effluents treated by fresh and used TX3-Db, respectively.

**Adsorption kinetics and isotherm experiments**

To evaluate the adsorption kinetics of the adsorbents, 0.25 g TX3-Db was added into 50 mL washing effluents with 1,000 mg/L PHCs at 25 °C. The concentration of PHCs in solution was measured by the gravimetric method at 1, 3, 5, 10, 20, 30 and 60 min, respectively.

The adsorption isotherm experiment was carried out in a series of 50 mL washing effluents with different concentration of PHCs (1,000, 2,500, 4,667, 6,500 and 8,833 mg/L). The controlled adsorption temperature was 25, 50, and 75 °C, respectively. The adsorption amount at time \(t\), \(q_t\) (mg/g), is expressed by the following Equation (4):

\[
q_t = \frac{(C_0 - C_t)V}{m}  \quad (4)
\]

The adsorption amount at equilibrium, \(q_e\) (mg/L), was calculated by the following Equation (5):

\[
q_e = \frac{(C_0 - C_e)V}{m}  \quad (5)
\]

where \(m\) is the mass of adsorbent (g); \(C_0\) is the PHCs initial concentration (mg/L); \(C_t\) is the PHCs concentration at time \(t\) (mg/L); \(C_e\) is the PHCs concentration at equilibrium (mg/L); \(V\) is the volume of washing effluents (L).

**RESULTS AND DISCUSSION**

**Adsorbents characterization**

The surface morphology of the D and TX3-Db was examined by SEM and is shown in Figure 1(a) and 1(b), respectively. It was clearly observed that sample D consisted of small plates with the thickness of approximately 2 μm, each of which was evenly full of pores of 300–500 nm in diameter (Figure 1(a)). Compared to the raw diatomite, the number of pores on the surface of modified diatomite significantly decreased, and numerous protrusions appeared on the diatomite surface after the chemical modification, indicating that the roughness of modified diatomite was increased (Figure 1(b)). The change of the surface morphology of D sample could be attributed to the surface modification of the sample by TX-100.

The FTIR analysis (Figure 2(a)) of D, TX3-Db and TX3-Db after adsorption was conducted to identify the main functional groups on the adsorbents surface. The spectrum...
of D showed that the main bands occurred at 1,620, 1,047, 802, and 623 cm\(^{-1}\). The band at 1,620 cm\(^{-1}\) could be ascribed to the H-O-H bending vibration (Sheshdeh \textit{et al.} 2014). Peaks at 1,047 cm\(^{-1}\) and 802 cm\(^{-1}\) were attributed to the Si-O asymmetric and symmetric stretching vibrations (Al-Ghouti \& Al-Degs 2011). And, the band of 623 cm\(^{-1}\) reflected the Si-O-Si bending vibration (Sheshdeh \textit{et al.} 2014). It is worth noting that a new band (1,456 cm\(^{-1}\)) was observed on TX3-Db, which was related to the saturated C-H stretching of the hydrophobic chain of TX-100 (Wang \textit{et al.} 2011). The appearance of C-H vibration peak gives the spectroscopic evidence of chemical modification of the diatomite surface, indicating that TX-100 was successfully grafted onto the diatomite surface. It is noted that, after adsorption, the peak intensity at 1,456 cm\(^{-1}\) was significantly reduced, which could be attributed to the surface structural adjustment of TX3-Db after adsorption of PHC molecules.

The XRD patterns of D and TX3-Db are shown in Figure 2(b). The diatomites mainly consist of crystalline phase cristobalite and quartz, and a weak diffraction peak was observed between 20\(^\circ\) and 22\(^\circ\), which indicated the appearance of the amorphous SiO\(_2\) in the diatomites (Zheng \textit{et al.} 2018). Also, the intensity of cristobalite phase was slightly weaker after the chemical modification, which might be attributed to the alkaline etching in the modification process.

The \(\text{N}_2\) adsorption/desorption and pore size distribution curves of natural and modified diatomite are shown in Figure 3. A rapidly increased adsorption amount was observed at relatively low pressures (<0.02), then a distinct hysteresis loop appeared at \(P/P_0\) in the range of 0.05–0.95, and finally the nitrogen adsorption sharply increased at
higher relative pressure (>0.95). The N$_2$ adsorption isotherms of D and TX3-Db could be categorized as type II curves based on the IUPAC (International Union of Pure and Applied Chemistry) classification (Al-Ghouti & Al-Degs 2011; Sheshdeh et al. 2014). The BET surface area of diatomite samples was greatly improved from 1.0 to 3.6 m$^2$/g after the modification (Table 1), which could provide more active sites for adsorption process. Also, the main pore size distribution of D and TX3-Db mainly ranged from 1 to 3 nm and 10 to 15 nm, respectively. The amount of the mesopores of TX3-Db largely improved compared to the D sample. Such obvious changes in the specific surface area and pore diameter were beneficial to the adsorption process.

The binding energy of TX3-Db and D was analyzed by XPS (Figure 4(a)), observing the peak of O1s (532.2 eV), C1s (284.8 eV) and Si2p (102.8 eV), respectively. It was observed from Figure 4(b) that the measured O/C atomic ratios increased from 3.37 (D) to 3.52 (TX3-Db) after the chemical modification. The increased O/C atomic ratios could be attributed to introduction of oxygen-containing functional groups such as ether bond and hydroxyl in TX-100 (Li & Ding 2006).

**Table 1** Textural properties of D and TX3-Db

<table>
<thead>
<tr>
<th>Sample</th>
<th>D</th>
<th>TX3-Db</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{BET}$ (m$^2$/g)$^a$</td>
<td>1.0</td>
<td>3.6</td>
</tr>
<tr>
<td>Vol (cm$^3$/g)$^b$</td>
<td>0.002</td>
<td>0.010</td>
</tr>
<tr>
<td>Average pore diameter (nm)</td>
<td>1.4</td>
<td>10.9</td>
</tr>
</tbody>
</table>

$^a$Specific surface area of BET.

$^b$Volume of mesopores.
Comparison of WE of natural and modified diatomite

WE was used to evaluate the recyclability of washing effluents. As clearly shown in Figure 5(a), WE of washing effluents regenerated by D, Db and TX3-Db with the concentration of 0.5 g/100 mL were 58.1, 66.7 and 76.5%, respectively. It can be seen that washing effluents treated by TX3-Db exhibited better WE compared with the alkali-treated diatomite Db and raw diatomite D. The washing effluents were regenerated after the selective adsorption of PHCs by adsorbents. Compared with the other two adsorbents, the much better regeneration capacity of TX3-Db for washing effluents depends on its hydrophobic and negative interfacial structure. The former is beneficial to the adsorption of PHCs, while the latter facilitates the retention of negatively charged micelles in washing effluents.

Adsorption capacity of TX3-Db

The adsorption capacity of TX3-Db was investigated and shown in Figure 5(b). It was observed that the adsorption amount of adsorbents rapidly increased at the initial adsorption stage (0–10 min), and then gradually achieved the plateau with the value of 560 mg/g. The equilibrium adsorption capacity \( q_e \) of adsorbents was also tested. A higher \( q_e \) value (560 mg/g) was obtained by TX3-Db compared to the raw diatomite with the value of 480 mg/g, which indicated that the adsorption capacity of modified diatomite could be largely promoted due to the changes in the surface structure and functional groups. The adsorption capacities of different adsorbents based on common natural inorganic minerals were summarized, as shown in Table 2. Bentonite and alumina showed a pretty low adsorption capacity with the values of 378, and 106.04 mg/g, respectively (Okiel et al. 2014; Franco et al. 2014). The reported diatomite-based adsorbents exhibited much higher adsorption capacity for the pollutants such as methylene blue, Pb\(^{2+}\), and petroleum (Khraisheh et al. 2004; Khraisheh et al. 2005). By contrast, modified diatomite adsorbent TX3-Db, developed in this study, exhibited the highest adsorption capacity, 560 mg/g. The TX3-Db also has the characteristic of selective adsorption which other reported adsorbents do not have. Obviously, this TX3-Db adsorbent has a unique advantage in the process of removing PHCs from soil washing effluents.

Adsorption kinetics

Pseudo-first-order (Equation (6)) and pseudo-second-order kinetic models (Equation (7)) (Franco et al. 2014) and linear driving force (LDF) model (Equation (8)) (Albertina et al. 2019) were used to illustrate the adsorption kinetics of PHC onto TX3-Db, which are embodied by the following equations:

\[
q_t = q_e (1 - e^{-k_1t})
\]

where \( q_t \) and \( q_e \) are the adsorption amount of adsorbents at time \( t \) and equilibrium (mg/g) respectively, \( t \) is the adsorption time, \( k_1 \) is the rate constant of the pseudo-first-order
**Table 2** | Comparison of adsorption capacities of different adsorbents

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Experimental conditions</th>
<th>Pollutants</th>
<th>Adsorption capacity (q&lt;sub&gt;e&lt;/sub&gt;) (mg/g)</th>
<th>Selective adsorption</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bentonite</td>
<td>C&lt;sub&gt;0&lt;/sub&gt;: 1,000 mg/L; Adsorbent dosage: 0.5 g/200 mL, Adsorption time: 4 h.</td>
<td>Petroleum</td>
<td>378</td>
<td>–</td>
<td>Okiel et al. (2011)</td>
</tr>
<tr>
<td>Alumina</td>
<td>C&lt;sub&gt;0&lt;/sub&gt;: 300 mg/L, Adsorbent dosage: 2.5 g/L, Adsorption time: 100 min, Temperature: 25 ℃, pH: 7.</td>
<td>Crude oil</td>
<td>106.04</td>
<td>–</td>
<td>Franco et al. (2014)</td>
</tr>
<tr>
<td>Diatomite</td>
<td>C&lt;sub&gt;0&lt;/sub&gt;: 100 mg/L, Adsorbent dosage: 0.05 g/50 mL, Adsorption time: 48 h, pH: 11.</td>
<td>Methylene blue</td>
<td>81.09</td>
<td>–</td>
<td>Khraisheh et al. (2005)</td>
</tr>
<tr>
<td>Modified diatomite</td>
<td>C&lt;sub&gt;0&lt;/sub&gt;: 300 mg/L, Adsorbent dosage: 0.05 g/50 mL, Adsorption time: 21 h, Temperature: 25 ℃, pH: 4.</td>
<td>Heavy metal (Pb&lt;sup&gt;2+&lt;/sup&gt;)</td>
<td>24.94</td>
<td>–</td>
<td>Khraisheh et al. (2004)</td>
</tr>
<tr>
<td>Modified diatomite</td>
<td>C&lt;sub&gt;0&lt;/sub&gt;: 2,500 mg/L, Adsorbent dosage: 0.5 g/100 mL, Adsorption time: 30 min, Temperature: 25 ℃.</td>
<td>PHC</td>
<td>560</td>
<td>Selective adsorption</td>
<td>This study</td>
</tr>
</tbody>
</table>

**kinetic model:**

\[ q_t = \frac{q_e^2}{1 + q_e \cdot k_2 \cdot t} \]  

where \( k_2 \) is the rate constant of pseudo-second-order kinetic model:

\[ \frac{dq}{dt} = k_{LDF}(q_e - \bar{q}) \]  

where \( \bar{q} \) is the average PHCs concentration on the TX3-Db, \( k_{LDF} \) is the rate constants of LDF model. Furthermore, \( \bar{q} \) is calculated from the mass conservation equation:

\[ C_0 V_L = CV_L + m \bar{q} \]  

where \( C_0 \) is initial PHCs concentration; \( C \) is residual PHCs concentration; \( V_L \) is volume of solution; \( m \) is mass of adsorbent.

The correlation coefficient (R<sup>2</sup>) of pseudo-first-order, pseudo-second-order and LDF models (Figure 6) was 0.935, 0.983 and 0.957. It can be concluded that the pseudo-second-order model fitted well with experimental data, with the highest correlation coefficient. Also, the calculated adsorption amount of pseudo-first-order kinetic model, pseudo-second-order kinetic model and LDF model was 466.6, 504.7 and 347.7 mg/g respectively (Table 3). Among them, the calculated adsorption amount of pseudo-second-order kinetic model was closer to the measured adsorption amount (560.0 mg/L). The obtained results showed that the adsorption of PHC on diatomite surface followed the pseudo-second-order model, suggesting the adsorption process was mainly the chemical adsorption (Li et al. 2020). Obviously, the surface structure of diatomite modified by TX-100 plays an important role in the adsorption of PHCs.

**Adsorption isotherms**

Langmuir and Freundlich models were used to explain the interactive action between the PHC and diatomite in the adsorption process. The two adsorption isotherm models can be embodied by the following equations (Alshammari et al. 2020):  

\[ q_e = \frac{q_{\text{max}} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \]  

\[ q_e = K_F \cdot C_e^{1/n} \]
Equations (10) and (11) correspond to Langmuir and Freundlich adsorption models respectively, where \( C_e \) is the concentration at equilibrium of pollutants (mg/L), \( q_e \) represents the equilibrium adsorption amount of adsorbents (mg/g), \( q_{\text{max}} \) is the maximum adsorption capacity of adsorbents, \( K_L \) is the Langmuir constant, \( K_F \) is the Freundlich constant, and \( n \) is an empirical constant.

Generally, the Langmuir model mainly illustrates the monolayer adsorption of molecules on a homogeneous surface, while the Freundlich model demonstrates the multilayer adsorption of molecules on heterogeneous surfaces (Amir et al. 2018; Abdul-Hameed 2019). Simulation curves of the two isotherm models are presented in Figure 7(a) and 7(b). The simulated parameters listed in Table 3.

<table>
<thead>
<tr>
<th>( q_{e,\exp} ) (mg/g)</th>
<th>( q_{e,\text{cal}} ) (mg/g)</th>
<th>( k_1 )</th>
<th>( R^2 )</th>
<th>( q_{e,\text{cal}} ) (mg/g)</th>
<th>( k_2 )</th>
<th>( R^2 )</th>
<th>( q_{e,\text{cal}} ) (mg/g)</th>
<th>( k_{\text{LDF}} )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>560</td>
<td>466.6</td>
<td>0.566</td>
<td>0.935</td>
<td>504.7</td>
<td>0.00156</td>
<td>0.983</td>
<td>347.7</td>
<td>0.19363</td>
<td>0.957</td>
</tr>
</tbody>
</table>

Figure 6 | The (a) pseudo-first-order and pseudo-second-order kinetic model; (b) LDF model. (adsorption conditions: adsorbent dosage = 0.5 g/100 mL, temperature = 25 °C).

Figure 7 | Adsorption isotherms of TX3-Db fitted by (a) Langmuir and (b) Freundlich model. (adsorption conditions: adsorbent dosage = 0.5 g/100 mL, time = 24 h).
Selective adsorption and regeneration by modified diatomite

Table 4 show that, compared with the Freundlich model, the Langmuir model was better fitted to the experimental data at 25, 50 and 75 °C, as shown by the higher correlation coefficient (R² > 0.95), suggesting the adsorption of PHC occurring on TX3-Db surface was mainly dominated by the monolayer adsorption process. Also, the dimensionless separation factor (R_L) of the Langmuir isotherm was expressed with the following Equation (12) (Okiel et al. 2011):

$$R_L = \frac{1}{1 + K_L C_0}$$  \hspace{1cm} (12)

where $C_0$ is the initial PHCs concentration in washing effluents (mg/L), $K_L$ is the Langmuir constant. Previous research (Seliem & Komarneni 2016) has demonstrated that the adsorption process was irreversible when the $R_L = 0$, adsorption was favorable when $0 < R_L < 1$, adsorption was linear when the $R_L = 1$ and adsorption was unfavorable when $R_L > 1$. As shown in Table 4, $R_L$ values were 0.199, 0.404, and 0.593, respectively at the different temperatures, suggesting the favorable adsorption of PHC by TX3-Db.

Optimization of adsorption parameters

Important parameters that affect WE of washing effluents regenerated by TX3-Db were optimized, including modifier dosage, adsorbent dosage, time and temperature, as shown in Figure 8. The WE curve of regenerated washing effluents showed a trend of rising first and then falling, with the maximum WE value at 3.0% TX-100 dosage (Figure 8(a)). Excessive TX-100 caused the decline of WE, which could be attributed to the agglomeration of hydrophobic chains on adsorbent surface (Khraisheh et al. 2004), which are channels through which PHCs diffuse from the surfactant micelles to the hydrophobic cores of the adsorbent. The variation tendency of influence of adsorbent dosage on the WE was similar to that shown in Figure 8(a). The WE value reached the highest when the TX3-Db was 0.50 g/100 mL and then decreased with the further increase of the TX3-Db (Figure 8(b)), which could be explained by the excessive adsorbent causing the precipitation and coagulation of TX3-Db. The influence of adsorption time on the WE is shown in Figure 8(c). It was obviously found that the WE increased when the adsorption time was less than 30 min, and maximum WE (76.5%) was obtained when the adsorption time was 30 min. However, WE slightly decreased when the adsorption time exceeded 30 min due to the desorption phenomenon (Khraisheh et al. 2004). The maximum adsorption amount could be achieved in a short period of time, which could shorten the adsorption process and improve the removal efficiency. Therefore, 30 min was regarded as the optimum adsorption time. The impact of adsorption temperature on the WE was also explored. It was observed from Figure 8(d) that the higher WE was obtained at the lower adsorption temperature. This phenomenon was closely related to the adsorption process occurring more easily at relatively lower temperature due to the adsorption of PHCs being an exothermic reaction (Caner et al. 2015).

Recyclability of washing effluent and adsorbent

The reusability of regenerated washing effluents and TX3-Db adsorbent was evaluated; the results are shown in Figure 9. The regenerative capacity of the washing effluents and the adsorbent was evaluated with the indicator of RE. It was observed that the RE value for washing effluents in three cycles is 94.7%, 84.2% and 78.9%, respectively. For TX3-Db adsorbent, the corresponding values were 94.7%, 78.9% and 63.1%, respectively. Obviously, washing effluents still maintained a high RE value after three reuses, suggesting that through the application of this kind of cheap and renewable adsorbent, TX3-Db, the recycle of washing effluents was realized, which greatly reduced the elution cost of surfactant-enhanced washing technology.

Selective adsorption mechanism

A selective adsorption mechanism is proposed to profoundly explore the fundamental removal process of PHCs from washing effluents, as shown in Figure 10. The reason for the decrease in the eluting efficiency of the washing effluents was that adsorption of PHCs by anionic–nonionic mixed surfactant micelles tended to saturation. The key to the selective adsorption of TX3-Db lies in its special structure of hydrophobic clusters and negative charge on its surface. In the adsorption process, the surfactant micelles
and PHCs molecules will be close to the adsorbent surface by hydrophobic interaction. Along the hydrophobic chain of the adsorbent, the PHCs are transferred to the hydrophobic core of TX3-Db. Since the negative charges were formed on the diatomite surface after the alkali pretreatment, under the action of electrostatic repulsion, the surfactant micelles with negative charge diffuse into the solution again, petroleum-loaded TX3-Db could be separated by centrifugation, finally resulting in the regeneration of washing effluents.

CONCLUSION

A cost-effective modified diatomite adsorbent was synthesized and used for the selective adsorption of PHCs in
the soil washing effluents. The optimal TX3-Db adsorbent with high adsorption capacity guarantees the regeneration of washing effluents. The adsorption process can be described by pseudo-second-order and Langmuir isotherm model. On the basis of revealing the structure–activity relationship, the selective adsorption mechanism, based on steric hindrance and electrostatic repulsion, was proposed to explain the removal of PHCs from washing effluents. The recycling technology of washing effluents, developed in this study, is of great significance for controlling the overall remediation cost of surfactant-enhanced washing technology.

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