Biosurfactant rhamnolipid enhanced modification of corn stalk and its application for sorption of phenanthrene

Le Tong, Weiting Liu, Weijia Lin, Chuling Guo, Jing Yang, Yanfu Wei, Yingying Xie, Shasha Liu and Zhi Dang

ABSTRACT

The application of modified agricultural wastes for removing polycyclic aromatic hydrocarbons (PAHs) from water is gaining a growing interest. However, most modified methods using synthetic chemicals may cause secondary pollution. To overcome this limitation, in this study, a rhamnolipid-modified corn stalk (RL-CS) for the removal of phenanthrene (PHE) from aqueous solution was prepared using a rhamnolipid-enhanced acid modification method. RL-CS with higher surface area and lower polarity exhibited higher PHE removal efficiency than that of raw corn stalk (RCS). The adsorption kinetics of RL-CS fitted well with pseudo-second-order kinetics ($R^2 > 0.999$). Sorption coefficients and carbon-normalized sorption coefficient of RL-CS were 4.68 and 2.86 times higher than that of RCS. Sorption process of RL-CS was nonlinear. Meanwhile, the sorption was an exothermic process and could occur spontaneously. The present study demonstrated that biosurfactant-modified biosorbent RL-CS may be of great potential for the removal of low concentrations of PAHs from the contaminated waters.

Key words | corn stalk, phenanthrene, rhamnolipid, sorption, wastewater treatment

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a group of aromatic hydrocarbons with two or more fused benzene rings, which have been considered to be priority pollutants by the United States Environmental Protection Agency (US EPA) (Menezes et al. 2015). PAHs are formed during the combustion of fossil fuels and biomass, and are widely present in surface water and ground water (Xi & Chen 2014). They are of low water solubility and resistant to mineralization. Different methods have been applied to remove PAHs from wastewater including chlorination, oxidation, ultrasonic irradiation, and adsorption (Changhaivong & Khaodhiar 2009). Among them, adsorption has shown advantages over other methods for removing PAHs from water at low concentrations owing to its environmental friendliness, low cost and high efficiency (Huang et al. 2006; Li et al. 2010; Tang et al. 2010; Yuan et al. 2010; Chen et al. 2011).

More and more researches focused on using agricultural wastes (e.g., chitosan, sugar cane bagasse and corn stalk) for remediation due to their low-cost and potential to be a source of biomass energy (Garg et al. 2008; Salim et al. 2010; Vafakhah et al. 2014). Corn stalk is one of the main crops in South China, which is mainly composed of cellulose, hemicellulose and lignin (Mahvi 2008; Hussein et al. 2009). Cellulose and hemicellulose are polar components of corn stalk, which can inhibit adsorbing PAHs, while lignin with relatively hydrophobic nature shows higher absorption capacity for PAHs than cellulose and hemicellulose (Sun et al. 2014). Concentrated acid solutions have been used to modify agricultural wastes (Huang et al. 2006; Chen et al. 2008; Li et al. 2010; Xi & Chen 2014). Acid hydrolysis could remove polar component and improve the adsorption capacity of agricultural wastes for PAHs. However, concentrated acids are toxic, hazardous and corrosive. Recently,
diluted acids were proved to be successful for pretreating lignocellulosic materials (Sun & Cheng 2002; Alivra et al. 2010). Therefore, diluted acids may replace concentrated acids to pre-treat lignocellulosic materials.

Cationic surfactant (hexadecyltrimethyl ammonium bromide) has been utilized to modify the rice stalk and fibric peat by ion exchange, which yielded a more hydrophobic surface and better affinity for PAHs (Tang et al. 2010; Zhang et al. 2015). However, the use of the artificially synthesized surfactants can cause secondary pollution. Nowadays, biosurfactants are very promising to replace synthesized surfactants because of their renewable resources, they are sustainable and biologically degradable, among which rhamnolipids (RLs) are often selected as the model one. RLs, as an anionic biosurfactant, are usually secreted by Pseudomonas aeruginosa with high interfacial activity, biodegradability and environmental compatibility (Asçi et al. 2008). Biosurfactants may interact with the corn stalk through forming hydrogen bonds with hydroxyl groups on the stalk surface and leave the nonpolar tails towards the water medium, thus increasing surface hydrophobicity of the corn stalk (Ivshina et al. 2015).

Therefore, our hypothesis was that combining with dilute acid pretreatment, RL enhanced modification of corn stalk could yield a more hydrophobic surface and better affinity for PAHs, resulting in high absorption of PAHs. The aims of the present study were as follows: (1) to modify and characterize the corn stalk with dilute hydrochloric acid combined with biosurfactant RL to obtain an efficient biosorbent for removing PHE; (2) to examine the adsorption characteristics of the modified corn stalks materials to elucidate the adsorption mechanism. Structural characteristics of raw corn stalk (RCS) and modified stalk were analysed by elemental composition, BET-N₂ surface area (SA), and Fourier transform infrared spectroscopy (FTIR). RL, one of the widely applied biosurfactants, was selected to further enhance the modification. Phenanthrene (PHE) was chosen as a model PAH because it was a common pollutant in the wastewater.

Materials and Methods

Materials

RCS was collected from a farm in Guangzhou, China. RCS was washed with fresh water, dried in natural conditions and crushed into granules. 0.18–0.42 mm size of granules was selected by sieving and placed in 60°C oven to constant weight, and stored in the dryer for use.

PHE was purchased from Sigma-Aldrich Chemical Company (98% in purity, USA). Methanol was obtained from ANPEL Laboratory Technologies (HPLC grade, Shanghai, China). RL was obtained from Zijin Biological Technology Co., Ltd (>90% in purity, Huzhou, China). The 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC), pyridine 4-(dimethylamino) pyridine (DMAP) was supplied by Aladdin Industrial Corporation (Shanghai, China). N,N-Dimethylformamide (DMF) was supplied by Tianjin Damao Chemical Reagent Factory.

Modification of corn stalk

Corn stalk was first treated with dilute hydrochloric acid (2% HCl) at 95°C for 3 h and then was washed with deionized distilled water to adjust these residues to neutral conditions. Next, acid corn stalk (HCS) was freeze-dried under vacuum. Hydrochloric acid corn stalk (1 g) was dipped in 100 mL DMF and bath sonicated for 1 h. Then 0.6 g RL was added into the suspension and stirred by glass rods until RL completely dissolved. Next, EDC and DMAP were added into the suspension and the chemical reaction was ongoing under stirring and sonication simultaneously to ensure adequate reaction for over 3 h. After that, the suspension was precipitated with methanol. The solid precipitate (RL-CS) was centrifuged and washed with anhydrous ethanol five times, and then with ultrapure water twice. Finally, RL functionalized corn stalk composite was freeze-dried under vacuum and used for adsorption and desorption. All reagents used in the above reaction were of analytical grade.

Characterization of corn stalk sorbents

The surface areas (SAs) of RCS, HCS and RL-CS were determined by an SA and porosity analyzer (NOVA4200e, Carl Zeiss) in order to study how SAs varied. All samples were degassed at 95–100°C for 24 h, prior to N₂ adsorption at –196°C. A thermal field emission environmental scanning electron microscope (SEM), Model (Carl Zeiss Jena Merlin, Germany), was used to examine the morphological changes of RCS and modified corn stalk. Before scanning, RCS, HCS and RL-CS were coated with a thin layer of gold using a sputter coater in a vacuum chamber. Elemental analysis (C, H, N, S) was conducted by instantaneous combustion using an Elementar Vario EL cube analyzer. This can help us study the content of elements and polarity of
Batch sorption studies

Sorption isotherms of PHE to raw and modified corn stalk (RCS, HCS and RL-CS) were obtained using a batch equilibration technique. The PHE solution was dissolved in methanol and then diluted using the background solution. The background solutions were composed of 0.01 mol L\(^{-1}\) CaCl\(_2\) and 200 mg L\(^{-1}\) NaN\(_3\), which maintained the ionic strength in water and minimized biodegradation of PHE by bacteria, respectively. The content of methanol is less than 0.1% of total solutions to avoid any co-solvent effects. Preliminary experiments were conducted to determine the amount of adsorbent to solution to ensure 30–70% uptake of initial PHE at apparent equilibrium. Raw and modified corn stalk (RCS, HCS and RL-CS) were placed in 20 mL Teflon-lined screw cap brown glass tubes with test solutions (50–1,000 \(\mu\)g L\(^{-1}\) PHE, pH = 7). The samples of each PHE concentration, including the control (without corn stalk), were run in triplicate. Glass tubes were shaken at 25 °C and 150 rpm for 24 h, which was long enough for equilibrium according to our pre-experiments. After centrifugation at 4,000 rpm \(^{-1}\) for 30 min, the supernatants were mixed with methanol (1:1, V: V) and filtrated through a 0.22-\(\mu\)m nylon membrane. PHE concentrations were detected by high performance liquid chromatography (HPLC). The adsorbed PHE by each biosorbent was calculated by mass difference in the control and sample.

Data analysis

Sorption data were fitted with two kinds of sorption isotherm models (Huang et al. 2006; Zhang et al. 2015).

The linear model:

\[
q_e = K_d C_e \tag{1}
\]

The Freundlich model:

\[
\log q_e = \log K_f + N \log C_e \tag{2}
\]

where \(q_e\) (mg kg\(^{-1}\)) is the amount sorbed per unit weight of sorbent. \(C_e\) (mg L\(^{-1}\)) is the equilibrium concentration; sorption coefficient \((K_d)\) was calculated from the slope of the linear isotherms. \(K_f\) ((mg kg\(^{-1}\))/ (mg L\(^{-1}\))^N) is the Freundlich capacity coefficient; and \(N\) (dimensionless) is the Freundlich exponent that describes isotherm nonlinearity.

Desorption hysteresis (Guo et al. 2014) was calculated as the ratio of Freundlich exponents for desorption \((N_{des})\) to sorption \((N_{ads})\) as:

\[
HI = \frac{N_{des}}{N_{ads}} \tag{3}
\]

RESULTS AND DISCUSSION

Characteristics of bioadsorbents

From SEM images, we can find out that the surface of RCS is relatively smoother with dense structure than 2% HCl corn stalk and 2% HCl-RL corn stalk. After being treated by 2% HCl, the surface of corn stalk turned curly and coarse with wrinkles appearing. On the basis of 2% HCl, RL-functionalized corn stalk has a rougher surface and more pores than 2% HCl corn stalk from Figure 1(c). Acid solution can remove the saccharide component (polar component), which inhibited agricultural wastes adsorption capacity of PAHs (Li et al. 2010). 2% HCl-RL functionalized corn stalk improved corn stalk adsorption capacity by increasing SA and porosity.

Table 1 shows elemental analysis, atomic rations and BET-N\(_2\) specific SA of the different corn stalk fractions. The content of carbon was in the order of HCS > RL-CS > RCS, the same trend as the content of hydrogen. The content of oxygen was in the order of RCS > RL-CS > HCS. It showed that dilute hydrochloric acid removed polar components of agricultural wastes. After being treated by HCl, the carbon content of corn stalk was increased by 17.01% and oxygen content of corn stalk was decreased by 19.69% compared with RCS. The carbon content of RL-CS was reduced by 7.48% and the oxygen content of RL-CS was increased by 8.43% compared with HCS. It indicated that ester group was formed after esterification between RL and HCS. We can speculate that carboxyl of RL and hydroxyl of HCS had chemical reaction by catalysis. HCS had the highest carbon content and the lowest oxygen content, and displayed highest aromaticity [(N + O)/C = 0.654]. RL-CS had the lowest atomic ratio H/C, which
indicated highest aromaticity. Overall, RL-CS had the largest SA and had more multiple adsorption sites than RCS and HCS.

FTIR spectrums of RCS, HCS, and RL-CS are shown in Figure 2(a) and 2(b). The large band was observed in three spectrums at about 3,410 cm⁻¹, which represents the stretching vibration of hydroxyl functional groups. The spectra of 2,920 cm⁻¹ and 897 cm⁻¹, two significant absorption peaks, represent the stretching vibration of C-H bond in asymmetric and symmetric aliphatic hydrocarbons, CH₂ and CH₃, respectively (Hussein et al. 2009; Abdullah et al. 2010). 1,630 cm⁻¹ is caused by flexural vibration of the absorbed water (Liu et al. 2006b). The small absorbance at 1,511, 1,460, and 1,320 cm⁻¹ correspond to the aromatic skeletal vibrations and ring breathing with C-O stretching in lignin (Sun et al. 2001). A strong band at 1,050 cm⁻¹ originates from C-O stretching in cellulose, hemicelluloses, and lignin or C-O-C stretching in cellulose and hemicelluloses (Rengasamy et al. 2011). A strong band at 897 cm⁻¹ is assigned to C₁-H bond bending vibrations of cellulose annular base and hydroxyl distorting vibrations (Liu et al. 2006a). FTIR spectra can confirm that corn stalk is mainly composed of cellulose, hemicellulose and lignin. Compared with spectrums between RCS and HCS, the absorbance of 2,920 cm⁻¹ and 1,250 cm⁻¹ disappeared after acid hydrolysis, which showed that wax of lignin was dissolved in

### Table 1  | Elemental analysis, atomic ratios and BET-N₂ specific SA of the different corn stalk fractions

<table>
<thead>
<tr>
<th>Sample</th>
<th>C%</th>
<th>H%</th>
<th>N%</th>
<th>S%</th>
<th>O%</th>
<th>(N + O)/C</th>
<th>H/C</th>
<th>SA, m² g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>RL-CS</td>
<td>42.10</td>
<td>6.184</td>
<td>1.11</td>
<td>0.123</td>
<td>50.483</td>
<td>0.922</td>
<td>1.763</td>
<td>2.265</td>
</tr>
<tr>
<td>HCS</td>
<td>49.58</td>
<td>7.351</td>
<td>1.02</td>
<td>0</td>
<td>42.049</td>
<td>0.654</td>
<td>1.779</td>
<td>0.716</td>
</tr>
<tr>
<td>RCS</td>
<td>32.57</td>
<td>4.826</td>
<td>0.77</td>
<td>0.097</td>
<td>61.737</td>
<td>1.442</td>
<td>1.778</td>
<td>0.102</td>
</tr>
</tbody>
</table>
solution and most of hemicellulose was hydrolyzed. Compared with spectrums between HCS and RL-CS, 2,920 cm\(^{-1}\) (\(-\text{CH}_3\)) appeared, which indicated that \(-\text{CH}_3\) may belong to RL and chemical reaction had taken place. The absorbance of 1,728 cm\(^{-1}\) (ester C\(=\)O) was not obvious, which suggested that esterification reaction occurred, while esterification rate may be very low.

### Adsorption kinetics

The adsorption kinetics showed that adsorption capacity changed over time and it displayed how adsorption happened. Figure 3(a) displays adsorption kinetics of three kinds of corn stalk. Adsorption kinetics of three corn stalk exhibited similar behaviours. The concentration of PHE on the three biomasses had a rapid increase as soon as the contact occurred during the first 8 h and then changed a little. Apparent adsorption equilibrium reached was at 24 h. The contact time of 24 h was sufficient for the equilibrium sorption and 24 h was used in the following sorption isotherms study.

In order to figure out adsorption kinetics of three materials and the underlying processes that control chemical reactions, pseudo-first-order kinetics and Lagrange pseudo-second-order kinetic model were used to fit adsorption kinetics data (Ho & McKay 1998). Table 2 shows the data. The kinetic equations, the initial sorption rate \((H, \text{mg g}^{-1} \text{h}^{-1})\), and the half-sorption time \((t_{0.5}, \text{min})\) were obtained using Equation (4)–(7), respectively.

\[
\log \left( \frac{q_e - q_t}{q_e} \right) = \frac{\log q_e - k_1 t}{2.303} \tag{4}
\]

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{t}{q_e} \tag{5}
\]

\[
H = k_2 q_e^2 \tag{6}
\]

\[
t_{0.5} = \frac{1}{k q_e} \tag{7}
\]

Here, \(q_e \, (\mu\text{g g}^{-1})\) and \(q_t \, (\mu\text{g g}^{-1})\) represent the amounts of PHE adsorbed by the sorbents at equilibrium, respectively; \(k_1 \, (\text{h}^{-1})\) and \(k_2 \, (\text{g mg}^{-1} \text{h}^{-1})\) are the rate constants of the pseudo-first-order and pseudo-second-order sorption, respectively. The initial sorption rate, \(H \, (\text{mg g}^{-1} \text{h}^{-1})\), can be determined from \(k_2\) and \(q_e\) values based on the method of Ho & McKay (1998). Also, half of the sorption time, \(t_{0.5}\), is the time required for the adsorbent to take up half as much PHE as it would have taken up at equilibrium \((t = t_{0.5} \text{ as } q_t = q_e/2)\) (Zhou et al. 2012).

Results showed that the adsorption process of three materials was in compliance with the Lagrange pseudo-second-order kinetic model, and has a good linear relationship \((R^2 \geq 0.999)\), indicating that the adsorption process may involve chemisorption (Rengasamy et al. 2011). The \(R^2\) values of the pseudo-second-order kinetic model \((0.999 \text{ for three biomasses})\) were higher than those of the pseudo-first-order kinetic model \((R^2, 0.73–0.76)\). The largest sorption rate \((k_2, 0.776 \text{ g mg}^{-1} \text{h}^{-1})\) was observed in the treatment of RL-CS, followed by HCS \((0.542 \text{ g mg}^{-1} \text{h}^{-1})\), and finally RCS \((0.527 \text{ g mg}^{-1} \text{h}^{-1})\). The \(k_2\) value of RL-CS is larger than RCS and HCS, and obtained the shortest half of the sorption time\((t_{0.5})\). The initial sorption rate \(H\) of RL-CS is
greater than that of RCS and HCS at the initial stage, and is nearly 6.85 times greater than that of RCS. The same trend was previously reported for the sorption of PHE onto HTAB-modified rice straw (Zhang et al. 2015). The $k_2$ value of RL-CS (1.293E-5 g μg$^{-1}$ min$^{-1}$) is larger than that of de-sugared pine wood (2.500E-6 g μg$^{-1}$ min$^{-1}$), de-sugared pine needles (2.333E-6 g μg$^{-1}$ min$^{-1}$), de-sugared pine bark (2.833E-6 g μg$^{-1}$ min$^{-1}$) and base hydrolysis of fungal biomasses of *Phanerochaete chrysosporium* (1.000E-5 g μg$^{-1}$ min$^{-1}$) (Xi & Chen 2014; Gu et al. 2015). The initial sorption rate $H$(150.083 μg g$^{-1}$ min$^{-1}$) of RL-CS is greater than that of base hydrolysis of fungal biomasses of *Phanerochaete chrysosporium* (48.962 μg g$^{-1}$ min$^{-1}$), RS (42.9 μg g$^{-1}$ min$^{-1}$), MRS-0.2 (42.7 μg g$^{-1}$ min$^{-1}$), MRS-0.5 (64.1 μg g$^{-1}$ min$^{-1}$), MRS-1.0 (128.2 μg g$^{-1}$ min$^{-1}$). These parameters indicated that RL-CS is a good potential material for adsorbing PHE.

To understand the PHE adsorption kinetics on three biomasses, the particle diffusion model was fitted with proposed data. If the resulting curves were through the origin of coordinates, it means that the controlling step of the adsorption process is only determined by the inter-particle diffusion (Ho & McKay 1999). Figure 3(d) shows the resulting three curves do not pass through the origin of coordinates, which indicates that the inter-particle diffusion is not the only controlling process. Adsorption rates were controlled by at least two steps, such as diffusion between the particles, membrane diffusion and adsorption on the surface of the solute (Ayoob et al. 2008).

### Table 2 | Pseudo-second-order kinetic parameters for PHE sorption on RCS, HCS and RL-CS

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>$q_e$, exp μg g$^{-1}$</th>
<th>$k_2$ (g mg$^{-1}$ h$^{-1}$)</th>
<th>$q_e$, cal μg g$^{-1}$</th>
<th>$t_{1/2}$ (min)</th>
<th>$R^2$</th>
<th>$H$ (mg g$^{-1}$ h$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RL-CS</td>
<td>3,337</td>
<td>0.776</td>
<td>3,406</td>
<td>22.7</td>
<td>0.999</td>
<td>9.005</td>
</tr>
<tr>
<td>HCS</td>
<td>1,856</td>
<td>0.542</td>
<td>1,850</td>
<td>59.8</td>
<td>0.999</td>
<td>1.855</td>
</tr>
<tr>
<td>RCS</td>
<td>1,542</td>
<td>0.527</td>
<td>1,579</td>
<td>72.1</td>
<td>0.999</td>
<td>1.314</td>
</tr>
</tbody>
</table>

![Figure 3](https://iwaponline.com/wst/article-pdf/76/5/1167/450554/wst076051167.pdf)
Modelling of adsorption isotherm

Adsorption isotherm of RCS, HCS and RL-CS are presented in Figure 4. Linear and Freundlich regression parameters are listed in Table 3. In addition, analysis showed that our data did not fit the Langmuir model well; thus, it is not shown in the paper. Sorption isotherms fit well with the Freundlich model and the linear model (Mutavdžić Pavlović et al. 2014). Freundlich equation reflected the heterogeneity of the corn stalk surface. The Freundlich $N$ value varied from 0.526 to 0.764, indicating that sorption isotherms of PHE on three biomasses were not simple linear distribution, but non-linear multi-level nonlinear adsorption. This result was consistent with Zhang’s research (Zhang et al. 2013). The nonlinear sorption isotherms were likely to be the result of π–π electron interaction between the PAH molecules and aromatic cores of corn stalk, $N$ value varied from 0.62 to 0.526 by hydrochloric acid hydrolysis, indicating that adsorption process turned to be more nonlinear. Freundlich exponent $N$ decreased with the increase of nonlinearity due to the existence of heterogeneous sorption sites, structure, and/or composition (Liu et al. 2010; Zeng et al. 2014). Other studies reported the nonlinear sorption of PAHs by pine sawdust, aspen wood and lignin (Huang et al. 2006; Xi & Chen 2014; Zhang et al. 2014).

$K_f$, Freundlich sorption coefficient and $K_{oc}$ (carbon content-normalized partition coefficients) (Liu et al. 2010) are good parameters to describe the sorption affinity between organic contaminants and sorbents. Log$K_f$ values were in the order of RL-CS, HCS, RCS, which is consistent with result of adsorption kinetic process. Concentration-dependent organic carbon-normalized sorption capacity ($K_{oc}$) was calculated by the content of the organic carbon of corn stalk and $K_d$ values at three equilibrium concentrations. $K_{oc}$ values were in the order of RL-CS, HCS, and RCS at different concentrations, which is consistent with the results of $K_f$. $K_{oc}$ values decrease with the increase of equilibrium concentration due to the nonlinear adsorption. In this study, RL-CS had the greatest $K_{oc}$ values and the lowest ratio of H/C (the highest aromaticity). RL-CS showed rougher surface and more pores, the largest SA (2.265) and aromaticity (1.763) than those of HCS and RCS (as shown in Table 1 and Figure 1), which may partly contribute to its high sorption capacity. The polarity index of RL-CS [(N + O)/C = 0.922] decreased 36% than RCS [(N + O)/C = 1.442]. These parameters showed that after modification, RL-CS was prone to adsorb more PHE. Compared with rice straw, $K_d$ and $K_{oc}$ value of RL-CS (7.846 L g$^{-1}$ and 19.304 L g$^{-1}$) is greater than that of MRS-1.5 (5.86 L g$^{-1}$ and 10.94 L g$^{-1}$), which indicated RL-CS has a better affinity for PHE than MRS-1.5 (Zhang et al. 2015).

**Effect of temperature**

In this study, we set the temperature gradient as 288, 298, 308 K to reveal the impact of temperature on the adsorption process.

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**Table 3** The parameters and correlation coefficients of linear and Freundlich isotherm models for the adsorption of PHE on three biomasses

<table>
<thead>
<tr>
<th>Sorbents</th>
<th>Linear equation</th>
<th>Freundlich equation</th>
<th>$K_{oc}$ (L g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_d$</td>
<td>$R^2$</td>
<td>$logK_f$</td>
</tr>
<tr>
<td>RL-CS</td>
<td>7,846.64</td>
<td>0.988</td>
<td>3.801</td>
</tr>
<tr>
<td>HCS</td>
<td>2,213.26</td>
<td>0.989</td>
<td>3.289</td>
</tr>
<tr>
<td>RCS</td>
<td>1,674.59</td>
<td>0.968</td>
<td>3.148</td>
</tr>
</tbody>
</table>

$R$ is regression coefficient. $K_{oc}$ is the carbon-normalized sorption coefficient ($K_{oc} = (K_f/f_{oc})/(C_a Ce)^{(N+1)}$) (Liu et al. 2010).
adsorption. Van’t Hoff equation was employed to describe the thermodynamic sorption properties of PHE (Aksu & Tunç 2005):

\[
\ln K_d = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}
\]

where \(K_d\) is the sorption coefficient which can be obtained from the linear regression of sorption isotherm (Equation (1)); \(R\) is the gas constant \((8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1})\); \(\Delta H\) and \(\Delta S\) are the standard enthalpy and entropy changes in sorption processes at a different temperature. The change of standard Gibbs free energy \((\Delta G)\) was calculated by Equation (9):

\[
\Delta G = -RT \ln K_d
\]

Results showed that when the temperature increased from 288 K to 308 K, sorbed PHE amount of RL-CS decreased Figure 5. High temperature was unfavorable for PHE adsorption. Thermodynamic parameters such as the standard enthalpy change \((\Delta H)\), standard entropy change \((\Delta S)\), and standard Gibbs free energy change \((\Delta G)\) were used to further demonstrate whether or not the sorption processes are exothermic and spontaneous. The data are shown in Table 4. When concentration of PHE varied from 0.015 mg/L to 0.40 mg/L, the \(\Delta G\) value varied from \(-6.046 \text{ kJ mol}^{-1}\) to \(-4.820 \text{ kJ mol}^{-1}\); \(\Delta H\) value was \(-23.797 \text{ kJ mol}^{-1}\); \(\Delta S\) value was \(-0.062 \text{ kJ mol}^{-1}\). Three parameters showed that adsorption process was exothermic and spontaneous.

The findings are consistent with results of previous studies. Schlautman & Morgan (1995) note that the adsorption capacity of the adsorbent decreases with increasing temperature for the vast majority of hydrophobic organic compounds. Distribution coefficient of most micropollutants decreased with temperature increasing (Ten Hulscher & Cornelissen 1996). Other studies have pointed out that the Henry constant will change by varying temperature, which affects the distribution and migration of PAHs in the environment. When the temperature rises 2°C, the Henry constant increases about 10% (Ten Hulscher et al. 1995), which revealed that adsorption process was exothermic (Gupta et al. 2010; Zhang et al. 2014).

### Desorption studies

Adsorption-desorption isotherm parameters of RL-CS absorbing PHE are shown in Table 5. Desorption isotherm showed to be significantly non-linear, which revealed desorption hysteresis existed. Desorption hysteresis was 0.887 calculated by desorption hysteresis coefficient \(HI\) count calculation method, namely Equation (3). Desorption hysteresis generally indicates that the adsorption process was irreversible. Therefore, the adsorption mechanism of PHE on RL-CS may be combined effect of a variety of mechanisms.

RL-CS absorbed PHE was desorbed in the background solution. From Figure 6, desorption rate ranged from 20%–40% and was relatively low, which indicated that the bond force was strong. The result was consistent with that obtained from adsorption-desorption isotherms. Results also showed that RL-CS had good stability and a strong impact resistance for absorbing PHE.

| Table 4 | Thermodynamic parameters for PHE absorbed by RL-CS |
| --- | --- | --- | --- | --- |
| T (K) | \(\Delta G\) (kJ mol\(^{-1}\)) | \(\Delta S\) (kJ K\(^{-1}\) mol\(^{-1}\)) | \(\Delta H\) (kJ mol\(^{-1}\)) | \(R^2\) |
| 288 | -6.046 | | | 0.972 |
| 298 | -5.111 | -0.062 | -23.797 | 0.965 |
| 308 | -4.820 | | | 0.976 |

| Table 5 | Parameters for adsorption and desorption isotherms |
| --- | --- | --- | --- | --- |
| Sorbent | Linear equation | Freundlich equation |
| --- | --- | --- | --- | --- |
| **Adsorption** | | | | |
| \(K_d\) (L g\(^{-1}\)) | \(R^2\) | \(\log K_f\) | \(N\) | \(R^2\) |
| 8.578 | 0.988 | 1.8506 | 0.7165 | 0.977 |
| **Desorption** | | | | |
| 7.0526 | 0.965 | 1.7413 | 0.6354 | 0.946 |
PAHs, which provide a new way for removing organic pollutants from aqueous solutions. After modification, modified corn stalk exhibited notable removal efficiency and its sorption coefficients were 4.68 times higher than those of the original fractions. Sorption process was non-linear, which indicated that π-π interaction may exist for the modified corn stalk. The adsorption kinetics fit well with pseudo-second-order kinetics. The particle diffusion model showed that adsorption rates were controlled by at least two steps (diffusion between the particles and membrane diffusion). Biosurfactant-modified corn stalk could be an alternative biosorbent for removing low concentration PAHs, which provide a new way for removing organic pollutants from contaminated environments.

CONCLUSIONS

The present study shows that biosurfactants enhanced by modification of corn stalk can be used as a biosorbent for removing PAH from aqueous solutions. After modification, modified corn stalk exhibited notable removal efficiency and its sorption coefficients were 4.68 times higher than that of the original fractions. Sorption process was non-linear, which indicated that π-π interaction may exist for the modified corn stalk. The adsorption kinetics fit well with pseudo-second-order kinetics. The particle diffusion model showed that adsorption rates were controlled by at least two steps (diffusion between the particles and membrane diffusion). Biosurfactant-modified corn stalk could be an alternative biosorbent for removing low concentration PAHs, which provide a new way for removing organic pollutants from contaminated environments.

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