Regeneration of Washing Effluents for Remediation of Petroleum-Hydrocarbons-Contaminated Soil by Corncob-Based Biomass Materials

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ABSTRACT: Surfactant-enhanced soil washing is an effective remediation method for petroleum-hydrocarbons-contaminated soil. The residual petroleum hydrocarbons in the washing effluents reduce the elution ability of the washing effluents and cause secondary pollution to the environment. In this work, modified corncobs were prepared and used as selective adsorbents to remove the residual petroleum hydrocarbons in washing effluents. The structure of adsorbent was characterized and the adsorption conditions were optimized. With the adsorption by corncob-based adsorbents, washing effluents can be regenerated and recycled. After five cycles, the recovery efficiency of the washing effluents is still as high as 75.4%. The optimal adsorbent linear alkylbenzene sulfonates (LAS-Cb) also exhibited excellent recyclability, which can be recycled five times. The selective adsorption mechanism of the LAS-Cb for petroleum hydrocarbons in washing effluents, related to its huge hydrophobic core and surface electronegativity, is proposed.

1. INTRODUCTION

Petroleum hydrocarbons in soils result in long-term contamination that poses potential hazard to human health and harm the ecosystem function. To remediate the petroleum-hydrocarbons-contaminated soil, more attention has been paid on surfactant-enhanced soil washing, owing to its relatively high washing efficiency (WE). In the engineering practice of remediation of petroleum-hydrocarbons-contaminated soil, washing soil with an aqueous solution of anionic–nonionic mixed surfactants has been considered to be the most promising method, owing to its better solubilization capacity for hydrophobic organic contaminants. Although surfactant-enhanced soil washing has been widely practiced as a preferred treatment option, in previous studies, little attention has been paid to the regeneration and reuse of washing effluents for remediation of petroleum-hydrocarbons-contaminated soil. Washing effluents that elute soil petroleum hydrocarbon, on the one hand, containing residual petroleum hydrocarbon, if not treated, are bound to cause secondary pollution to the environment. On the other hand, if the washing effluents are not recycled, the surfactant in the washing effluents will be wasted, resulting in a significant increase in remediation costs. Therefore, the regeneration of washing effluents, both for protecting the environment and for reducing the cost of washing, has important practical significance.

The key to the recycling of washing solution is to remove the residual petroleum hydrocarbons. Recently, some technologies have been developed to remove organic pollutants from aqueous solutions, so as to realize the regeneration of washing effluents. Among these techniques of washing solution recovery, adsorption is an important alternative for its high efficiency, lower cost, and easy operation.

Previous studies have demonstrated that activated carbon, as an excellent adsorption material, has been widely used to remove organic pollutants in water. However, there are two obvious disadvantages for the activated carbon, for washing effluents regeneration may confine its application to a great extent: (i) the high cost for the preparation and regeneration and (ii) lack of selective adsorption ability, which is easy to cause the co-sorption of hydrophobic petroleum hydrocarbon and surfactant molecules on the surface of the activated carbon. Consequently, the purpose of this study is to develop a low-cost adsorption material which can be applied for the selective adsorption of petroleum hydrocarbons from the washing effluents for the remediation of petroleum-contaminated soil, thus leading to the regeneration and recycling of washing effluents.

Recently, the removal of pollutants from wastewaters by biosorption with agricultural wastes has attracted more attention because of their abundance and economic viability. Some studies showed that corncob, mainly composed of lignin, the polysaccharides cellulose and heme-
cellulose, exhibited excellent adsorption performance. Further researches revealed that the adsorption capacity of cellulosic waste materials can be greatly improved by proper chemical modification. At present, corncob-based adsorbent materials have been widely used for the removal of heavy metal ions, organic dyes, and nitrate. There are few researches on corncob-based adsorbents removing petroleum hydrocarbons from washing effluents for petroleum-hydrocarbons-contaminated soil.

In this work, a novel corncob-based adsorption material was prepared and used to remove the petroleum hydrocarbons from the soil-washing effluents, thus it provides a recyclable washing effluent to wash the petroleum-hydrocarbons-contaminated soil. When the corncob-based adsorbent is added into the soil-washing effluents, the petroleum hydrocarbons are selectively adsorbed on the surface of the corncob-based adsorbent. By centrifugation, the petroleum-loaded adsorbent is removed, resulting in the formation of regenerated washing effluents. As a result, the regenerated washing effluents can be further used to wash the petroleum-contaminated soil. With the help of the corncob-based adsorbent, we can recycle the washing effluent at least five times. To the best of our knowledge, this is the first time that recycling of washing effluents for petroleum-hydrocarbons-contaminated soil is achieved by corncob-based adsorbents.

2. RESULTS AND DISCUSSION

2.1. Characterization of the Prepared Adsorbents. The scanning electron microscopy (SEM) micrographs of the prepared adsorbents (C, Cb, and LAS-Cb) are shown in Figure 1. Compared with C, Cb and LAS-Cb exhibit flourishing pore structures. Previous research has reported that alkaline hydrolysis can cause the disruption of the lignin structure. Therefore, these generated pores can be attributed to the chemical reaction during pretreatment processes.

The nitrogen adsorption/desorption isotherms of C, Cb, and LAS-Cb are shown in Figure 2. The adsorption isotherms of C and Cb are very similar and display a type IV with hysteresis loops corresponding to type H4 from nitrogen adsorption/desorption isotherms, indicating slit-shaped mesoporous characteristics. It is noteworthy that the adsorption isotherm of LAS-Cb exhibits a type IV isotherm with an H3 hysteresis loop, which is obviously different from those of C and Cb. The results of specific surface area and volumetric adsorption measurements of the adsorbent are shown in Table 1. It can be seen that textural properties of corncob have been greatly changed after modification with LAS. Specific surface areas, total pore volumes, and average pore diameter increase by about 3.4, 5, and 1.4 times compared to C. The fact that the increase of pore volumes matches up with the observations in Figure 1.

The surface roughness of the three corncob-based adsorbents was characterized by an atomic force microscope (AFM). As shown in Figure 3a, C and Cb show a relatively smoother surface compared with LAS-Cb. Some granule-like

Figure 1. SEM images for C (a), Cb (b), and LAS-Cb (c).

Figure 2. Nitrogen adsorption/desorption isotherms (main plot) and pore size distribution curves (inset) of C, Cb, and LAS-Cb.

Table 1. Textural Properties of Adsorbents

| adsorbents | $S_{BET}$ (m$^2$/g)$^a$ | vol (cm$^3$/g)$^b$ | average pore diameter (nm) |
|------------|---------------------|--------------------|--------------------------|
| C          | 2.768               | 0.002              | 1.861                    |
| Cb         | 2.468               | 0.003              | 1.876                    |
| LAS-Cb     | 9.395               | 0.010              | 2.688                    |

$^a$Brunauer–Emmett–Teller (BET) specific surface areas. $^b$Total pore volumes.
microstructures were observed on the surface of LAS-Cb. Based on the analysis of the synthesis process of LAS-Cb, these granule-like microstructures can be attributed to the surfactant layer grafted on the corncob surface. The measured surface roughness (Ra) of the three adsorbents increases in the following order: C (1.10 nm) < Cb (2.21 nm) < LAS-Cb (3.76 nm), suggesting that alkali treatment and surfactant grafting modification increase the surface roughness, among which, surfactant grafting causes the most significant changes in the surface roughness.

The surface wettability of the three corncob-based adsorbents was investigated by contact angle measurement. As can be seen in Figure 3b, the contact angle of C, Cb, and LAS-Cb was 44.9, 63.2, and 82.2°, respectively. The changes of contact angle can be attributed to the change of the surface structure of the adsorbents. The highest contact angle was observed on the surface of LAS-Cb, suggesting that hydrophobicity of the LAS-Cb was significantly enhanced after grafting anionic LAS surfactant on the surface of the corncob.

The Fourier transform infrared (FT-IR) spectra of C, Cb, and LAS-Cb are shown in Figure 4. It is noted that the absorption band characteristic of the glucosidic ring at 897 cm⁻¹ can be observed in all adsorbent spectra, suggesting that the structure of the glucosidic ring remains intact after the chemical modification of natural corncob. The peak at 1404 cm⁻¹ is ascribed to O–H deformation vibration in the phenolic hydroxyl group of lignin. It can be seen that, after the alkali pretreatment, the peak intensity corresponding to phenolic hydroxy for Cb and LAS-Cb becomes weak, which can be attributed to the consumption of phenolic hydroxy due to the reaction with alkali. After LAS grafting treatment, a new peak appears at 1107 cm⁻¹ on the surface of LAS-Cb, which corresponds to the C–S stretching vibration of LAS. This result indicates that LAS has been successfully grafted onto the surface of the corncob.

2.2. Optimization of Adsorption Conditions. The LAS-Cb was used to optimize the adsorption conditions, including surfactant (LAS) dosage on the corncob, adsorbent dosage, adsorption time, and temperature. As can be seen in Figure 5a, the washing efficiency (WE) of regenerated effluents increases gradually with increasing the surfactant dosage on the corncob until it reaches a maximum value with a surfactant dosage of 5%. Further improving surfactant dosage (>5%) may lead to the blockage of mesopores on the corncob, reducing the number of active sites on the surface and finally causing the decline of washing efficiency of regenerated effluents. Figure 5b, a similar variation tendency was also observed for the effect of adsorbent dosage on the washing efficiency (WE) of regenerated effluents. WE values were 60.5, 62.1, 71.9, 67.6, and 64.4% for the dosage of 0, 0.25, 0.5, 0.75, and 1.0 g/100 mL, respectively. In the initial stage, the increasing dosage of adsorbents had a dramatic positive impact on WE, while a further increase of the adsorbent dosage (>0.5 g/100 mL) led to the decline of WE. It could be attributed to the coagulation and precipitation of LAS-Cb at higher concentrations. Adsorption time is another important variable affecting adsorption efficiency. Figure 5c exhibits the WE of regenerated effluents at different adsorption times. WE first increased with the increase of adsorption time. At 30 min, WE reached its maximum at 71.9% and then decreased slightly. Therefore, the optimum adsorption time was selected as 30 min. The effect of temperature on the adsorption of petroleum hydrocarbons by LAS-Cb was also investigated. The results are illustrated in Figure 5d. It was observed that the WE decreased from 71.9 to
64.3% as the adsorption temperature increased from 25 to 75 °C. This result exhibited that the adsorption of petroleum hydrocarbons from washing effluents is an exothermic process.28

2.3. Recyclability Performance. The regeneration capacity of the washing effluents was investigated, and the results are shown in Figure 6. The recovery efficiency (RE) of the washing effluent was used to evaluate its regeneration capacity. The RE of the fresh washing solution is defined as 100%. It can be seen that the RE value for adsorbent C is up to 80.7%. This indicates that the corncob itself has a regeneration capacity for the washing effluents. The regeneration capacity of washing effluents can be further improved when the corncob is treated with alkali or modified with a surfactant. The RE value for Cb and LAS-Cb is 83.8 and 96.9%, respectively. The regenerative washing ability of washing effluents results from the adsorption removal of petroleum hydrocarbons by adsorbents. The excellent regeneration capacity of LAS-Cb for washing effluents may be related to its high hydrophobicity and negative surface charge. The former is beneficial to the adsorption of petroleum hydrocarbons in washing effluents, whereas the latter is beneficial to keep negatively charged anionic–nonionic mixed micelles in washing effluents through electrostatic repulsion.

The washing performances of regenerated effluents treated with and without an adsorbent are compared, as shown in Figure 7. It can be seen that the RE value of washing effluents that are recycled directly without treatment is 61.5, 33.7, 8.4, 0, and 0%, respectively. By contrast, the corresponding values of washing effluents that are treated with the adsorbent (LAS-Cb) are 97.5, 94.8, 88.7, 80.9, and 75.4%, respectively. The results show that adsorbent LAS-Cb plays a significant role in restoring the washing efficiency of regenerated effluents. With the help of the adsorption of LAS-Cb, the recycling of washing effluents is realized. After five cycles, the RE value of the washing effluents is still as high as 75.4%. The excellent recyclability of the washing effluent treated with adsorbent...
could be explained by the following reason that the petroleum hydrocarbons in micelles could be removed by the corncob-based adsorbent (i.e., LAS-Cb), providing the regenerated adsorption capacity of the anionic–nonionic mixed micelles. Therefore, washing effluents could be recycled. In addition, multiple uses of washing effluents will greatly reduce the cost of remediation of petroleum-contaminated soil by the commonly used surfactant-enhanced washing method.

The recyclability of adsorbent (LAS-Cb) was also evaluated (see Figure 8). The recovery efficiency (RE) of the washing effluent regenerated by LAS-Cb was used to reflect the recyclability of LAS-Cb. It can be seen that the RE value in five cycles is 94.9, 86.7, 82.1, 80.1, and 74.9%, respectively. After LAS-Cb was reused five times, its RE value was still up to 74.9%, suggesting that the prepared LAS-Cb has excellent recyclability.

2.4. Selective Adsorption Mechanism. To better understand the excellent selective adsorption capacity of LAS-Cb for petroleum hydrocarbons in washing effluents, a selective adsorption mechanism is proposed, as shown in Figure 9. The reason why washing effluents lost their ability to wash the petroleum-contaminated soil was that anionic–nonionic mixed micelles have absorbed petroleum hydrocarbons and reached saturation. The mechanism of selective adsorption of petroleum hydrocarbon in washing effluents by adsorbent LAS-Cb lies in its unique structure: a huge hydrophobic core and negative charges on the surface. When the adsorbent LAS-Cb is added into the washing effluent, LAS-Cb adsorbent and the petroleum-loaded micelle attract each other, and then the petroleum hydrocarbon molecules migrate to the hydrophobic surface of LAS-Cb driven by hydrophobic–hydrophobic interactions. Afterward, the negative nonionic mixed micelles and negatively charged petroleum-loaded LAS-Cb were separated by electrostatic repulsion. Finally, the regenerated micelle diffused into the bulk solution, becoming an active component of the washing solution again, and the petroleum-loaded LAS-Cb was removed by centrifugation.

Thus, by virtue of the selective adsorption role of LAS-Cb, the petroleum hydrocarbons are selectively separated from washing effluents and enriched on LAS-Cb surface. After subsequent centrifugation, LAS-Cb adsorbed with petroleum hydrocarbons can be separated from the washing effluents. The regenerated washing effluent still contains a large number of effective anionic–nonionic mixed micelles, which can be used again to remediate petroleum-hydrocarbons-contaminated soil with high washing efficiency.

3. CONCLUSIONS

Corncob-based adsorbents were prepared to adsorb residual petroleum hydrocarbons from washing effluents. The optimal adsorbent LAS-Cb exhibited excellent selective adsorption performance for petroleum hydrocarbons. The selective adsorption capacity of LAS-Cb can be attributed to its unique structure: hydrophobic core and surface electronegativity. By virtue of the selective adsorption role of LAS-Cb, washing effluents can be recycled and reused five times. This result has important significance in the remediation of petroleum-hydrocarbons-contaminated soil: the cost for remediation will be greatly reduced; secondary contamination caused by washing effluents can be successfully avoided.

4. MATERIALS AND METHODS

4.1. Materials. Natural corncob was collected from Tianjin (China). Anionic surfactant (linear alkylbenzene sulfonates, LAS), sodium hydroxide, and Triton X-100 (TX-100) were purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). Other chemicals such as concentrated sulfuric acid, deionized water, and distilled water were obtained from Tianjin Huadong Reagent Factory (Tianjin, China).
4.2. Preparation of the Corncob-Based Adsorbent. Corn cob powder (C) was sieved to 180 μm and dried at 100 °C before use. The preparation of LAS-modified corn cob (LAS-Cb) was carried out by the following procedures: 20.0 g of C was slowly added into 200.0 mL of sodium hydroxide aqueous (0.6 M) with mechanical stirring at room temperature for an hour. After that, the solid phase in this solution was obtained and then dried at 50 °C to obtain alkali-treated corn cob (Cb). The obtained Cb was then added into 80.0 mL of LAS aqueous solution with suitable ration under stirring, treated by ultrasonic for 10 min, and then washed with distilled water and dried at 100 °C to generate LAS-Cb. All of the adsorbents were stored at room temperature in air.

4.3. Characterization of the Adsorbent. The morphological characterization of the prepared adsorbent was studied by scanning electron microscopy (SEM) taken on Shimadzu SS-550 at 15 kV. The surface roughness of the adsorbent was observed by an atomic force microscope (AFM) taken on Agilent Technologies AFM-S500. Fourier transform infrared (FT-IR) spectra of the adsorbent were recorded on a Bruker Tensor 27 spectrometer. Nitrogen adsorption/desorption (FT-IR) spectra of the adsorbent were recorded on a Bruker.

4.4. Preparation of Soil-Washing Effluents. Petroleum-hydrocarbons-contaminated soil with 22 wt % content of hydrocarbons was obtained from the suburb of Dongying city (China), which has been dried in air for a few years. The collected petroleum-hydrocarbons-contaminated soil was first screened through a 0.1 mm sieve and the concentration of petroleum hydrocarbons in the soil was determined by gravimetric method. The fresh washing solution containing LAS, TX-100, and sodium silicate was prepared according to the reported studies. Briefly, the mixed surfactant solution was first prepared by using a mass ratio of LAS to TX-100 of 3.1. The fresh washing solution containing LAS, TX-100, and sodium silicate was prepared according to the reported studies. The mixed surfactant solution was prepared by mixing LAS and TX-100 in the ratio of 3:1. The mixed surfactant solution was prepared by mixing LAS and TX-100 in the ratio of 3:1. The solution was then centrifuged at 3000 rpm for 30 min and the supernatant was used as the soil-washing solution to obtain the fresh washing solution.

The preparation of the soil-washing effluents was performed as follows: 3.0 g of petroleum-hydrocarbons-contaminated soil was added into 100.0 mL of the fresh washing solutions (with 0.3 g of surfactant) under continued stirring for about 20 min. After that, this solution was heated at 75 °C for an hour under magnetic stirring in a water bath. This solution was then centrifuged at 3000 rpm for 30 min and the supernatant was used as the soil-washing solution to perform the adsorption experiment again.

4.5. Adsorption Experiment. In the adsorption experiment, 0.5 g of the adsorbent was added into 100.0 mL of the soil-washing solution. The solution was stirred for 30 min at room temperature (25 °C) and then it was centrifuged at 3000 rpm for 8 min. The supernatant was collected and used as the regenerated washing effluent in our work. And then, the regenerated washing effluent was further used to wash the petroleum-hydrocarbons-contaminated soil. The washing efficiency (WE) was given by

\[
WE = \frac{c_1 - c_2}{c_1} \times 100\%
\]

where \(c_1\) is the concentration of petroleum hydrocarbons in the unwashed petroleum-hydrocarbons-contaminated soil and \(c_2\) is the concentration of petroleum hydrocarbons in the washed petroleum-hydrocarbons-contaminated soil. In addition, recovery efficiency (RE) was used to reflect the washing capacity of regenerated washing effluents and it can be calculated by using the following equation

\[
RE = \frac{WE_2}{WE_1} \times 100\%
\]

where \(WE_1\) is the WE of the fresh washing solution and \(WE_2\) is the WE of the regenerated washing effluent.

To investigate the recyclability of the washing effluent, the reuse experiment of the washing effluent was performed for five cycles. During these five cycles, 100.0 mL of the washing effluent was reused continuously five times, and the adsorbent was removed from the washing effluent after each cycle by centrifugation, prior to re-adding the unused adsorbent (0.5 g) into the washing effluent in the next cycle. All other experimental conditions and procedures were the same as those of the adsorption experiment. Similarly, the reuse experiment of the adsorbent was also carried out for five cycles to investigate the recyclability of the adsorbent. During these five cycles, 0.5 g of the adsorbent was reused continuously five times and 100.0 mL of the new soil-washing effluent was used in each cycle. All other experimental conditions and procedures were the same as those of the adsorption experiment. It should be noted that all of the recycle experiments were studied in triplicate.

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**Notes**

The authors declare no competing financial interest.

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