



Sorption of crude oil by enzyme-modified corn stalk vs. chemically treated corn stalk



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ARTICLE INFO

Article history:

Received 26 October 2017

Received in revised form 28 January 2018

Accepted 30 January 2018

Available online 1 February 2018

Keywords:

Enzymatic modification

Alkaline hydrogen peroxide

Oil spill

Sorption

ABSTRACT

To reduce the growing menace of oil pollution on the environment and health by sorption, much attention has been paid to the production of high performance materials with modified surfaces. In this study, the sorption of crude oil, often spilled on water, was achieved using corn stalk treated with different modifiers. Corn stalk was chemically modified with alkaline hydrogen peroxide (AHCS) and compared with corn stalk enzymatically modified with cellulase R10 (RCCS) and AC (ACCS) to improve the oil sorption capacity. All sorbents were fully characterized by FT-IR, XRD, BET and SEM, and the effects of different experimental factors, such as sorbent dosage, initial oil amount, and sorption time, on the sorption capacity were studied. All modified corn stalks showed a high and rapid oil sorption, and ACCS had the highest sorption capacity, which indicated that enzymatic modification exhibited better performance than chemical modification. The monolayer chemisorption of oil was predominant for all sorbents, and the Langmuir maximum sorption capacity was close to the experimental value, which was in the order of ACCS > RCCS > AHCS (27.03, 20.08 and 16.16 g/g, respectively). These results demonstrated that corn stalk modified by both cellulase and alkaline hydrogen peroxide could be considered to be an efficient and “green” material to remediate oil spills.

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1. Introduction

A large amount of plant biomass wastes (PBW) is produced by the agricultural industry, which is commonly discarded or ignited, causing serious environmental pollutions [1]. Due to the abundance and renewability, many researches have focused on the exploitation of PBW, among these value-added utilizations, producing biosorbent is the most important path to environmental protection. PBW is composed of cellulose, hemicellulose and lignin, which show high sorption capacities towards heavy metals ions, dyes, and organic pollutants in wastewater. Biosorbents derived from PBW are low-cost sorbents and can also solve waste disposal problems [2].

According to a report by NASA, over 700 millions of gallons of oil end up in the oceans each year via several routes, and oil spills are a devastating sources; for example, the Arabian Gulf spill during the Gulf War in 1991 and the Gulf of Mexico spill in 2010 are the top two marine oil spills to date [3,4]. Spilled oil endures complex weathering processes, including spreading, evaporation, emulsification, dispersion, photochemical oxidation and so on, which makes oil cleanup more difficult. Therefore, a more effective and immediate cleaning technique should be developed to minimize the damage caused by oil spill. Compared to other approaches to clean up spilled oil [5–8], the use of biosorbents is an eco-friendly and effective and has thus attracted growing research interests. Oil sorbent made from PBW can absorb oil from the oil/water surface by capillary forces and van der Waals forces. Many researchers have investigated a great variety of PBW, such as sawdust, kapok, sisal, cotton and sugarcane bagasse, as oil sorbents [2,9,10]. Among these materials, some raw agricultural products, such as milkweed, kapok, peat, cotton, and wool, which contain a large number of waxes and lipids on their outer surface and provide large areas for trapping and retaining oil, can absorb 15–40 times more oil than their own

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weight, which is 1.5–3.0 times greater than commercial synthetic sorbents [11–13]. Considering the economy and availability, other raw agricultural wastes, such as sugarcane bagasse [14], rice husk [15], corn straw [16], have shown good substitutability. However, they have lower sorption capacities (only 2–6 $\text{g}_{\text{oil}}/\text{g}_{\text{sorbent}}$), and they show weak hydrophobicity, which means large water volumes are taken up at the same time; hence, these materials must be treated by various methods to enhance their sorption capacities and hydrophobicity. The literature shows that carbonization [17,18], acetylation [19,20], grafting by fatty acid [21,22], modification by surfactant [23], and autohydrolysis [24] are commonly used, which significantly increase the oil sorption capacity. After acetylation, banana fibre can absorb oil from 2.1 to 18.12 g/g [25], and the sorption capacity of sawdust grafted by fatty acids was enhanced from 3.77 to 6.40 g/g [21].

Corn is a major economic crops worldwide, and it produces a variety of byproducts, such as corncobs, corn leaves and corn stalks [26,27]. In China, the annual production of corn stalk is 1.22–1.27 million tons; therefore, the utilization of this abundantly available and inexpensive resource is advantageous. The usage of corn stalk as an oil-sorbent in the recovery of spilled oils has received attention recently [1,16]. Considering that the oil sorption capacity of raw corn stalk is relatively low, some modification methods are necessary to produce high-efficiency oil sorbents. The use of enzyme-based biotechnology in the modification process can save energy and reduce the use of toxic and environmentally harmful chemicals, but few studies have reported on the use of enzymatic modification to produce sorbents [28]. Previous studies by the authors found that the hydrolytic enzyme cellulase has the ability to partially hydrolyze cellulose, leading to improved swelling of the fibers, which enabled oil molecules to easily enter the cellulosic material, yet no systematic reports have been published [29]. Therefore, it is necessary to further investigate the production of oil sorbent by cellulase modification. In addition, based on a previous report, hydrogen peroxide can act as a delignifying agent. Treating PBW with H_2O_2 at a pH in the range of 11.2 to 11.8, causes the lignocellulosic substrates to partially delignify to produce low-crystalline materials [30]. According to previous research, this chemical procedure, which utilizes nontoxic reagents, could be an effective method to modify lignocellulosic substrates for enhancing the oil sorption capacity. However, the use of alkaline hydrogen peroxide (AHP) to modify corn stalk to produce an oil sorbent has not been studied.

To investigate and compare the effect of enzymatic and chemical modifications to produce oil sorbent, raw corn stalk (RCS) was chemically treated by AHP and enzymatically treated using two kinds of cellulase (R10 and AC). Using scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) spectroscopy and X-ray diffraction (XRD) analysis, good evidence of physical and chemical structural changes in the modified corn stalk was found, which can explain the mechanism for the enhancement of the oil sorption capacity. The main factors that influence the oil sorption capacity (OSC) were studied, i.e., the sorbent dosage and initial oil amount. This work utilized pseudo-first-order, pseudo-second-order and intra-particle diffusion kinetic models to describe the sorption process, and the Langmuir and Freundlich adsorption models were also used to analyze the sorption equilibrium isotherms.

2. Materials and methods

2.1. Materials

Raw corn stalk (RCS) was collected from a local farm in Guangzhou, China. After being air-dried for 2 weeks, the RCS was washed to remove dusts and impurities, dried at 60 °C, and then crushed to particles using a Willy mill. The fraction between 0.25 and 0.85 mm was selected by sieving.

Chemicals and reagents were purchased from Guangzhou Chemical Reagent Co. Ltd. (China). Crude oil (density at 20 °C = 0.852 g/cm,

viscosity = 0.028 Pa/s) from Sinopec (Guangzhou, China) was used in the experiment. Cellulase from *Aspergillus niger* (AC) was obtained from Sigma-Aldrich, USA, and Cellulase R-10 (RC) was received from Yakult, Japan. The activities specified by manufacturer were 0.57 and 10 units mg^{-1} solid, respectively. One unit liberates 1.0 μmol of glucose from cellulose in 1 h at pH 5.0 at 37 °C, which was used without further purification.

2.2. Oil sorbents preparations

2.2.1. Chemical modification of corn stalk by alkaline hydrogen peroxide

The alkaline hydrogen peroxide-modified corn stove (AHCS) was prepared by soaking 5 g RCS in 500 mL of distilled water containing 1% (w/v) H_2O_2 , while slowly stirring at room temperature for 14 h, and the pH was adjusted to 11.5 using NaOH. After reaction, the solution was neutralized with HCl. The samples were centrifuged and washed three times with distilled water to remove surface retained chemicals. Finally, the modified corn stove was dried in an oven at 60 °C until reaching a constant weight.

2.2.2. Enzymatic modification of corn stalk by cellulase

Cellulases including AC and RC were used as modifiers. Modification of RCS by AC was performed in a solution of 50 mM sodium acetate buffer at pH 4.5. At an enzyme loading of 100 U/g substrate, the reaction was carried out in a shaking water bath at 45 °C for 6 h, followed by heating the reaction system at 85 °C for 10 min to stop the enzyme reaction. After the solid residues were centrifuged and filtered, the precipitates were washed with plenty of distilled water and dried to a constant mass [29]. The final samples received were labeled as ACCS.

An RC solution with a concentration of 0.5 g/L was prepared using 50 mM sodium acetate buffer at pH 4.8. Raw corn stalk (5.0 g) was deposited in the 100 mL RC solution at 50 °C and shaken for 4 h. The enzyme action was stopped by heating the reaction system at 85 °C for 10 min. After the enzymatic modification, the samples were centrifuged and filtered, followed by thoroughly washing with distilled water and dried at 60 °C until constant mass. The final samples received were labeled RCCS.

2.3. Characterization of the oil sorbents

2.3.1. Surface functional group determination using FT-IR

After the chemical and enzymatic modifications, AHCS, ACCS and RCCS were scanned by a Spectrum One FT-IR from 500 to 4000 cm^{-1} (PerkinElmer, USA). FT-IR analysis can identify possible functional groups present on the surface of the samples.

2.3.2. Crystallinity measured by XRD

X-ray diffraction of the raw and modified corn stalks was performed using a Rigaku D/max-III A diffractometer (Rigaku Co. Japan). All samples were scanned over a 2θ angle range of 10° to 40°. The crystallinity index (CrI) of the sample was used to compare the impact of cellulase and AH on the lignocellulose, and CrI was calculated by Segal's equation [31]:

$$\text{CrI} = \frac{I_{002} - I_{\text{am}}}{I_{002}} \times 100 \quad (1)$$

where I_{002} is the maximum intensity of the 002 peak at $2\theta = 22.5^\circ$, and I_{am} is the lowest intensity of the amorphous area at $2\theta = 18.7^\circ$.

2.3.3. Scanning electron microscopy (SEM)

To compare the effects of enzymatic and chemical modification, the morphology and structure of all sorbents were inspected by SEM (Model S-3700N, HITACHI) at different magnifications. Before scanning, RCS, AHCS, ACCS and RCCS were coated with a thin layer of gold using a sputter coater in a vacuum chamber.

2.4. Oil sorption methods

2.4.1. Batch sorption experiments

Crude oil was selected for investigating the effects of the experimental parameters. An oil solution was prepared in a 400 mL beaker containing 150 mL distilled water with a given amount of oil under constant stirring. The oil sorption onto modified sample was performed at different dosage (0.1, 0.2, 0.3, 0.4, 0.5 g), initial oil amount (5, 10, 15, 20, 25, 30 g), and contact time (1, 3, 5, 10, 20, 30, 40, 50, 60, 70 min) in batch experiments. The sample was introduced into a steel wire mesh and then immersed in oil solutions at room temperature. When the sorption reached equilibrium, the sample was lifted up and drained for 5 min. The sample was weighed before and after oil sorption. After draining, the sample was dried at 60 °C in an oven for 24 h, and water content was the difference between the weight of the sample before and after drying [32].

$$\text{Oil sorption capacity} = (\text{TS} - \text{WS} - \text{DS}) / \text{DS} \quad (2)$$

where DS is the dry weight of the sorbent (g), TS is the total weight of the sorbent after sorption (g) and WS is the sorption capacity of water (g). All experiments were conducted in triplicate.

2.4.2. Sorption kinetic models

To elucidate the crude oil sorption kinetics of the enzymatically and chemically modified corn stalks, pseudo-first-order, pseudo-second-order and intra-particle diffusion models were utilized [33,34].

The pseudo-first-order kinetic model equation [35] is expressed as

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

The pseudo-second-order kinetic model equation [36] is expressed as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

$$t_{1/2} = \frac{1}{k_2 q_e} \quad (5)$$

$$h = k_2 q_e^2 \quad (6)$$

The intra-particle diffusion kinetic model equation [36] is expressed as

$$q_t = k_i t^{0.5} + C \quad (7)$$

where q_e and q_t (g/g) refer to the amount of oil sorbed per unit weight of biosorbent at equilibrium and time t , respectively, and k_1 and k_2 are the rate constants (1/s). The value of k_1 can be calculated from the slopes of the linear plot of $\log(q_e - q_t)$ versus t . The value of k_2 can be calculated from the slopes of the linear plot of $\frac{t}{q_t}$ versus t . $t_{1/2}$ and h specify the equilibrium adsorption in half the time and the initial sorption rate. k_i is the intra-particle diffusion coefficient, and C is the diffusion constant related to the thickness of the boundary layer.

2.4.3. Sorption equilibrium models

To examine the effect of the modification of corn stalk by enzymatic and chemical methods on the oil sorption capability, the Langmuir and the Freundlich isotherm models were adopted to analyze the sorption mechanism of the oil sorbent systems [35].

The Langmuir isotherm model represents a monolayer sorption system, and the linear form of the Langmuir isotherm equation is expressed as:

$$\frac{C_e}{q_e} = \frac{1}{b q_{max}} + \frac{C_e}{q_{max}} \quad (8)$$

$$R_L = \frac{1}{1 + b C_0} \quad (9)$$

The Freundlich isotherm model represents multilayer sorption on a heterogeneous surface. The corresponding linear form of the Freundlich isotherm model equation is expressed as:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (10)$$

where q_e and q_{max} (g/g) refer to the amount of oil sorbed per unit weight of biosorbent at equilibrium and the maximum sorption capacity defined theoretically, respectively, and C_e and C_0 (g/L) represent the equilibrium and initial concentration of oil in solution. b is the Langmuir constant, and R_L is the separation coefficient related to the attractive force between the oil and sorbent surface. $\frac{1}{n}$ and K_f are the Freundlich constants related to the sorption intensity, which can be calculated from the slope of the linear plots of $\ln q_e$ versus $\ln C_e$ [37].

3. Results and discussion

3.1. Comparison of the sorbent characteristics

3.1.1. Effect of chemical and enzymatic modification on the functional groups

The FT-IR spectra of raw and modified corn stalk are given in Fig. 1 (a). At first glance, all four spectra look similar. The strong and broad adsorption peaks at 3430 cm^{-1} are due to the O—H stretching vibrations, which occurred in cellulose. The peaks at 2921 cm^{-1} are assigned to C—H stretching. These two peaks are sharper in the spectra of RCCS and ACCS than in that of RCS. The peaks located at approximately 1735 cm^{-1} are attributed to C=O stretching of the acetyl and uronic ester groups, and this peak did not reduce in intensity for RCCS, ACCS or AHCS, which indicates that chemical and enzymatic modification couldn't weak ether bonding between the lignin and carbohydrates. The absorbances at 1340 cm^{-1} were attributed to the phenolic hydroxyl group in hemicellulose, and the peaks in the spectra of RCCS and ACCS were sharper than that in the spectrum of RCS, but the band in AHCS was weakened. These results suggested that AHP modification could remove some part of the hemicellulose, but cellulase modification could not digest hemicellulose [11,38,39].

The peaks related to aromatic skeletal vibrations in lignin at 1637 cm^{-1} and OH group vibrations in lignin at 1051 cm^{-1} were sharper in both cellulase-modified corn stalk samples than those in RCS and AHCS. Meanwhile, at 1250 cm^{-1} (assigned to ether groups) and 1540 cm^{-1} (attributed to aromatic ring C=C vibrations in lignin), the cellulase-modified corn stalk also showed the same trend [40–43]. Thus, based on these peaks, it could be concluded that after the cellulase reaction, the properties of cellulose changed, but the reaction had no effect on lignin, and thus, the relative amount of lignin increased; after the alkaline hydrogen peroxide modification, the compositions of hemicellulose, cellulose and lignin in corn stalk were all modified, and these results were in agreement with the determination of the component content (data not shown).

3.1.2. Effect of chemical and enzymatic modification on crystallinity changes

To explore the impact of chemical and enzymatic modification on crystallinity, the CrI, which can be calculated by Eq. (1), was used to

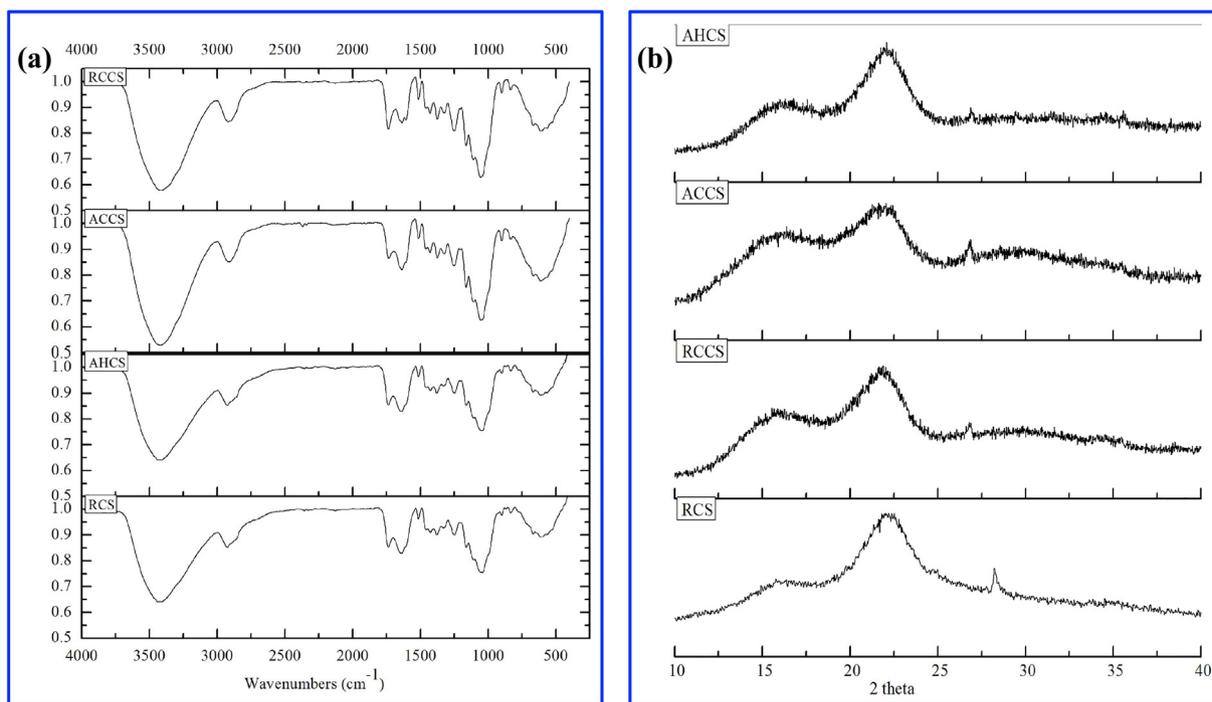


Fig. 1. Characterization of modified and unmodified corn stalk using (a) FI-IR and (b) XRD.

measure the degree of crystallinity of RCS, AHCS, RCCS and ACCS. The spectra of corn stalk obtained before and after each modification are shown in Fig. 1b, and the results are listed in Table 1.

It can be found that the treatment of corn stalk by both methods lowers the value of CrI, but the decrease was significantly different for the chemical and enzymatic methods. The cellulase-treated corn stalk, regardless of whether RC or AC was used, showed a significantly decrease in the CrI, and the CrI of ACCS was the lowest at 25.7%. However, the chemical treatment of corn stalk by alkaline hydrogen peroxide only showed a slight decrease (from 46.8% to 42.5%). The main reason was that cellulase can dissolve both of amorphous and crystalline cellulose; meanwhile, cellulase had no effect on lignin, which is deemed to be amorphous. On the other hand, chemical reagents can hardly enter the crystalline regions of cellulose, so that AHP rarely influences the change in crystallinity. ACCS had the lowest CrI and the largest surface area, so it possessed the best capacity of oil sorption, which illustrates that cellulase can facilitate the improvement of oil sorption.

3.1.3. Effect of chemical and enzymatic modification on the morphology and structure

SEM analysis was employed to observe the morphology and structural changes of corn stalk for comparison of the effect of different conversions. As shown in Fig. 2, the outer surface of RCS presented a compact rigid structure (Fig. 2a), and the inner surface consisted of a tightly compacted spongy region (Fig. 2b).

Cellulase treatment altered the complex structure in corn stalk because cellulase has the selective ability to breakdown cellulose, leading to the partial depolymerization of the recalcitrant structure of lignocellulose. The inner surface of corn stalk was significantly changed after AC

and RC treatment. Cellulase expanded the inner spongy region with the layer structure shown, and numerous small pores were present, which provide more sorption sites for oil molecules. Fig. 2 clearly shows that less destruction occurred on the exterior surface owing to the major non-cellulose, materials including lignin, wax and hemicellulose, in this area, and neither AC nor RC had the capacity to degrade them.

Compared to the cellulase modifications, the chemical treatment by AHP resulted in disruption of the outer surface of the corn stalk (Fig. 2g). This treatment can oxidate the whole lignocellulose substrate, and the significant difference was that AHP can partially delignate the corn stalk [44]. The SEM images of AHCS showed a pocked structure on its outer surface (Fig. 2h), which can hold oil.

3.2. Comparisons of the oil sorption performance

The oil sorption capacities of chemically and enzymatically modified corn stalk with different dosages in the range of 0.1–0.5 g were investigated, and the results are shown in Fig. 3(a). Oil uptakes ranged from 13.43 to 24.98 g/g for ACCS, from 14.1 to 16.9 g/g for RCCS and from 12.21 to 14.08 g/g for AHCS. The oil sorption efficiency of all sorbents enhanced simultaneously with increasing dosages from 0.1 to 0.2 g, and for ACCS and AHCS, a further increase in sorbent dose reduced the sorption capacity per unit sorbent. With respect to RCCS, the oil sorption capacities slightly increased as the dosage increased from 0.2 g to 0.3 g, and the oil uptake decreased slowly. The initial increasing trend can be explained by the increase in surface area (more active adsorption sites available) with the increase in adsorbent mass. At certain oil amounts, increasing the sorbent dose decreases the sorption capacity per unit sorbent, which occurs because an increase in the sorbent surface areas may lead to aggregation. As the sorbent aggregates, the total surface area may decrease, diffusional holes may be blocked, and sorption sites may be unsaturated [45].

The initial oil amount is a critical factor that influences the sorption capacity of the sorbent. In this work, oil sorption by ACCS, RCCS and AHCS was carried out for initial oil amounts in the range of 5–30 g/150 mL. The results are shown in Fig. 3(b), and the overall trend was that the OSC gradually increased with rising oil amounts. At a low initial oil amount (5 g), oil sorption was relatively low by all

Table 1
Characteristics of modified and raw corn stalk.

Sorbent	CrI (%)	Surface area (m ² /g)
RCS	46.8	2.31
ACCS	25.7	9.37
RCCS	26.9	7.86
AHCS	42.5	7.14

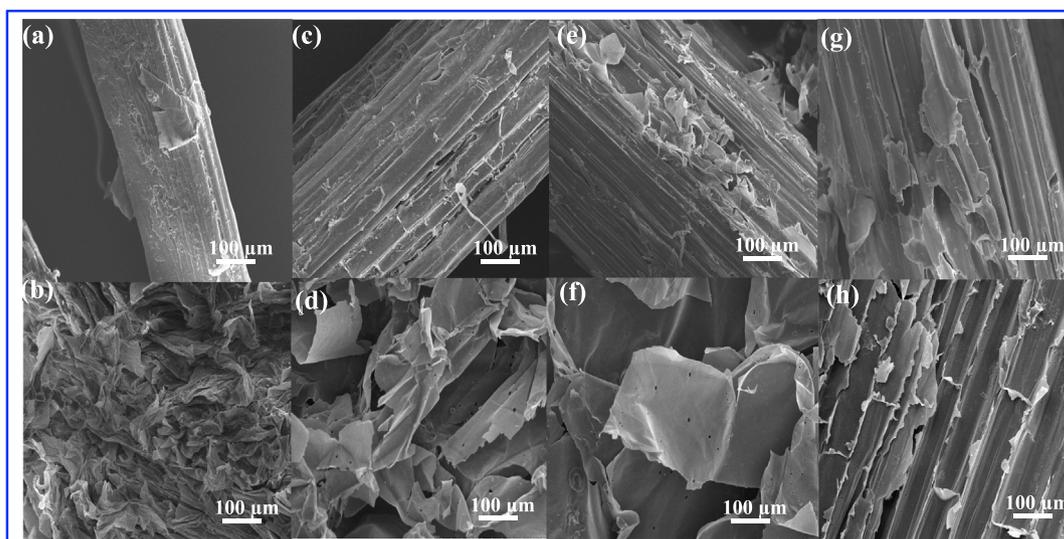


Fig. 2. Morphology and structural characteristics of (a, b)RCS, (c, d)ACCS, (e, f) RCCS and (g, h) AHCS. Magnification is 500 \times .

sorbents (12.38 g/g for ACCS, 9.23 g/g for RCCS and 8.73 g/g for AHCS). This may be due to that the water molecules were competed with the oil molecules for sorption sites on these sorbents. The lower the oil amount, the more sites that are occupied by water molecules; hence, there were fewer sites for oil absorption, leaving oil molecules in solution. Nevertheless, the sorption capacity of oil sharply increased for ACCS, RCCS and AHCS when increasing the initial oil amount from 10 to 20 g, and there was no significant change between 25 and 30 g. At high oil amount (30 g), the input of oil increased, and the competition from water decreased, so that more sites were available for oil molecules. The removal of oil is heavily dependent on the initial oil concentration; the more concentrated the solution, the better the adsorption [46]. Among all modified corn stalk, the oil sorption of ACCS and RCCS were better than that of AHCS, and the maximum oil sorption for ACCS, RCCS and AHCS was 24.98, 17.06 and 14.25 g/g, respectively.

The OSC depends on the surface area and the properties of the sorbent. The results of this research suggested that the enzymatically modified corn stalk exhibited a better OSC than chemically modified corn stalk, and the effect of the corn stalk modification was highly influenced by the source of cellulase. AC showed merit in hydrolyzing both

crystalline and amorphous cellulose [29], and thus, ACCS had the highest OSC, with the largest surface area and lowest CrI. RC can only affect 1,4- β -D-glycosidic bonds and hardly breaks down crystalline cellulose. AHP led to a lower lignin content but barely affected cellulose [44], and hence, AHCS had a relatively higher CrI than RCS, as the surface of the stalk formed an etching trench, which could hold oil molecules. To summarize, compared to RCS, corn stalk modified by both cellulase and alkaline hydrogen peroxide can uptake oil efficiently.

3.3. Sorption kinetics

Experiments were performed at certain time intervals to find the equilibrium time to obtain the maximum OSC by ACCS, RCCS and AHCS. The dynamic oil sorption of both the enzymatically and chemically modified corn stalks is shown in Fig. 4(a). In accordance with the trend in the chart, we can see that the sorption equilibrium time for ACCS is approximately 10–20 min, and that for RCCS and AHCS is approximately 5–10 min. The high rate of oil sorption implies that utilizing these sorbents allows for the treatment of much larger volumes of spilled oil at the same time with a subsequent savings in cost. For all

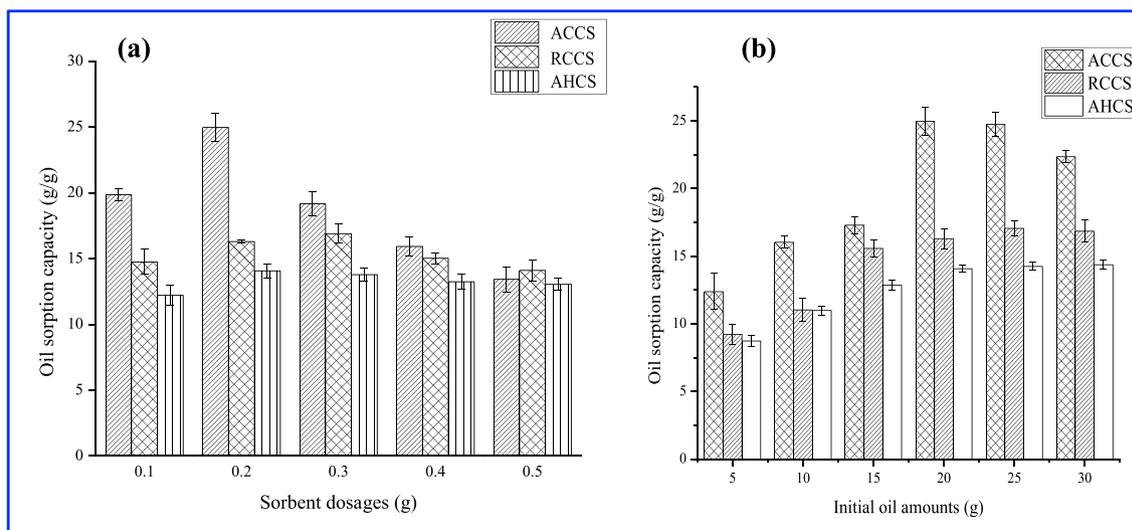


Fig. 3. Effect of (a) sorbent dosage and (b) initial oil amount on the sorption capacity of oil by ACCS, RCCS and AHCS.

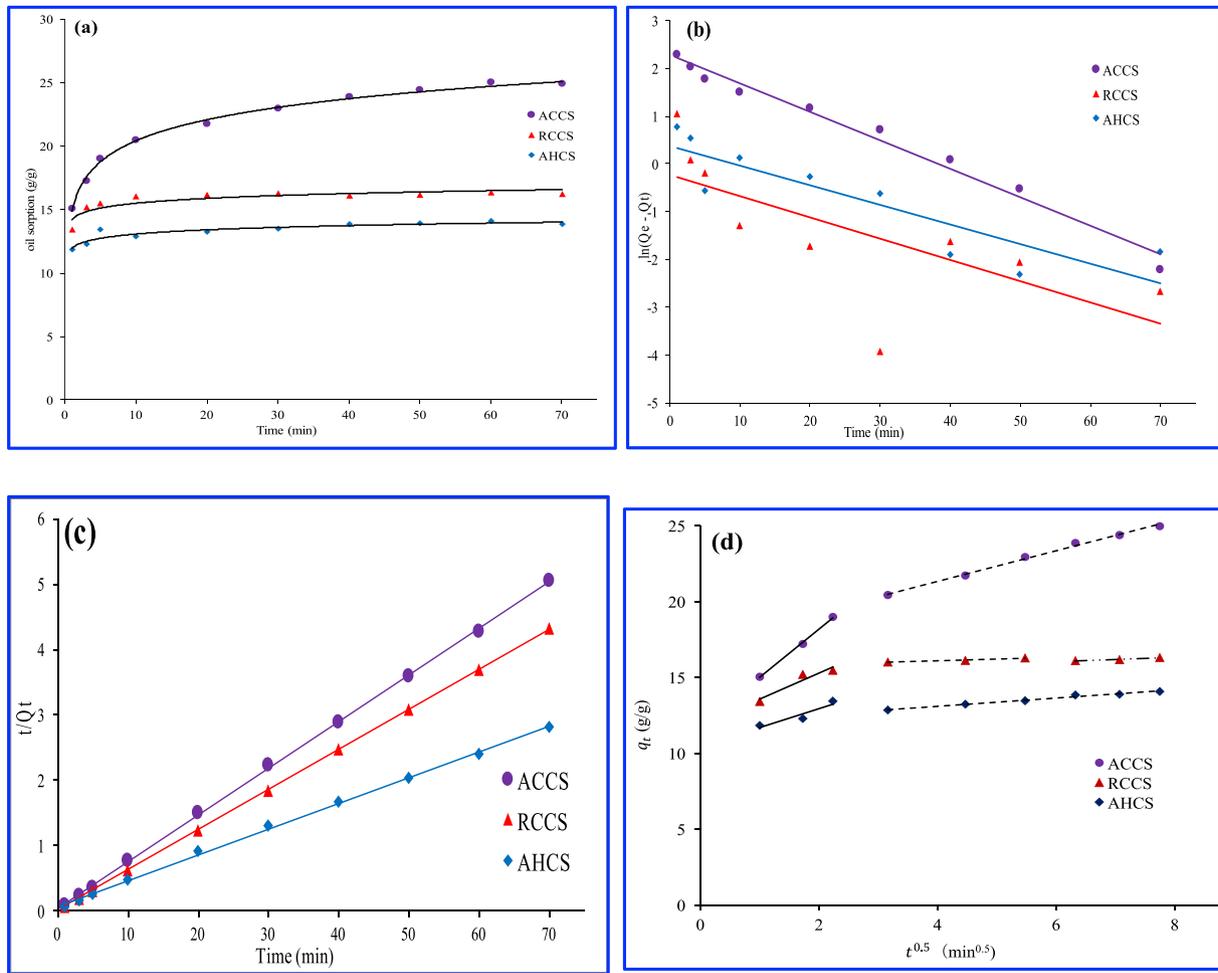


Fig. 4. Sorption kinetics of crude oil to (a) effect of contact time (b) pseudo-first order model (c) pseudo-second order model (d) intra-particle diffusion model.

kinds of sorbents, the sorption capacity increased rapidly during the first 5–10 min, which may due to the availability of sufficient sorption sites on the surface of the modified corn stalks. As the surface is occupied by oil molecules and becomes exhausted and saturated, the rate of oil sorption tends to drop off over sorption time.

The sorption process involves the mass transfer of crude oil from the liquid phase to the surface of the modified corn stalk. The pseudo-first-order, pseudo-second-order and intra-particle diffusion models were used to describe the oil adsorption process. The linear fitting plots of all sorption kinetic models are shown in Fig. 4 (b)–(d). The linear regression coefficient of determination (R^2) and parameters of the pseudo-first-order and pseudo-second-order kinetic models were calculated and are listed in Tables 2–4. The results showed that the pseudo-second-order model could explain the sorption process of oil on ACCS, RCCS and AHCS better than the pseudo-first-order model since the correlation coefficients R^2 were all above 0.999, and the

experimental $q_{e,Exp}$ values agreed well with the estimated q_{eq} values calculated from the pseudo-second-order equation. Therefore, it might be inferred that crude oil is chemically sorbed onto the sorption sites on all modified corn stalks. The data in Table 2 showed that the equilibrium sorption capacities of the biomass modified by cellulase AC and RC were higher than AHCS, and the rate constant k_2 can be established as follows: $RCCS > AHCS > ACCS$. To further discuss the overall chemisorption process, the equilibrium adsorption in half the time ($t_{1/2}$) and the initial sorption rate (h) are presented in Table 3. The half adsorption time can be reached by RCCS and AHCS more quickly, and that of RCCS was faster than AHCS. The initial sorption rates (h) of RCCS and AHCS were higher than that of ACCS, which has the same order as k_2 . Although the values of h and k_2 of RCCS and AHCS were higher than those of ACCS, their OSC values were lower. This phenomenon may be ascribed to a process in which a fast initial step, limited by diffusion, is followed by a slower second step (limited by diffusion in smaller pores or by lower specific surface area) [47], because both RCCS and AHCS had a lower specific surface area than ACCS. The OSC is proportional to the surface area of the sorbent (given in Table 1), which was in the order of $ACCS > RCCS > AHCS > RCS$.

Table 2
Parameters of the pseudo first- and second-order kinetics for oil adsorption.

Sorbent	$q_{e,Exp}$ (g/g)	Pseudo-first-order equation			Pseudo-second-order equation		
		q_{eq} (g/g)	k_1 (1/min)	R^2	q_{eq} (g/g)	k_2 (g/(g.min))	R^2
ACCS	24.98	9.845	0.0596	0.9813	25.45	0.019	0.9987
RCCS	16.3	0.8024	0.1025	0.5014	16.29	0.28	1
AHCS	14.08	1.455	0.0944	0.7814	14.01	0.12	0.9997

Table 3
The half adsorption time.

Sorbent	ACCS	RCCS	AHCS
$t_{1/2}$ (min)	2.068	0.2192	0.5948
h (g/g.min)	12.079	74.361	23.269

Table 4
Parameters of the intra-particle diffusion equation.

Sorbent	First Linear region			Second Linear region			Third Linear region		
	C	k_i	R^2	C	k_i	R^2	C	k_i	R^2
ACCS	11.824	3.1782	0.9973	17.288	1.0096	0.9947	/	/	/
RCCS	11.856	1.7133	0.9176	15.657	0.1105	0.9572	15.204	0.1399	0.9604
AHCS	10.451	1.2455	0.8802	12.005	0.2726	0.9828	/	/	/

The major disadvantage of the pseudo-second-order model is that it is not suitable for the diffusion process. To reveal the diffusion model of oil molecules in porous materials either by pore diffusion or solid surface diffusion, the intra-particle diffusion model was applied, and the sorption process may include two or three stages [34,48,49]. The larger the intercept, the larger the contribution of surface sorption in the rate-controlling step [36,50]. Fig. 4(d) showed the plots of q_t versus $t^{0.5}$. The plots were not linear over the entire time range and didn't pass through the origin, implying that multiple processes controlled the sorption. For ACCS and AHCS, two well-differentiable regions of oil sorption were observed, indicating that two different sorption mechanisms occurred. The first linear region may represent superficial layer diffusion, attributed to the diffusion of oil through the bulk solution to the external layer of the sorbent. Higher diffusion constants (C) indicate that the outer layer diffusion could be important for oil sorption. The second linear region may represent faster sorption due to the formation of oil layers on the surface of the sorbent, followed by inner diffusion, which represents permeation of the oil from the surface to the inner pores of the sorbent and has the slowest rate. The overall sorption process of RCCS include three stages, in which outer layer diffusion occurred during the first linear region, oil adhered to the sorption site on the surface of RCCS in the second linear region, and the third linear region refers to inner diffusion. The value of k_i indicates the rate of diffusion, which means a lower k_i value refers to a slower sorption process. As seen in Table 4, the values of k_i in all stages generally decreased in the order of ACCS > AHCS > RCCS, which corresponded to the decreased diffusion of crude oil from the exterior layer of sorbent and through the inner pores, respectively. For each stage, one could observe that the diffusion from bulk solution to the exterior layer of sorbent, which started in the first 5 min, was faster. The following portions of the plot seemed to indicate intra-particle diffusion with a lower rate, which implied that the intra-particle diffusion of oil was the rate-limiting step in the entire sorption process, but intra-particle diffusion was not the unique limiting step in terms of sorption speed, as the straight line didn't pass through the origin.

Table 5
The parameters of the Langmuir and Freundlich equations for oil sorption.

Sorbent	Langmuir				Freundlich		
	$q_{max}(g/g)$	$b(L/g)$	R_L	R^2	n	K_f	R^2
ACCS	27.03	0.0397	0.1589	0.9436	3.273	5.157	0.8477
RCCS	20.08	0.0339	0.1812	0.9832	3.139	3.463	0.9131
AHCS	16.16	0.0483	0.1344	0.9978	3.978	4.083	0.9675

Table 6
Comparison of OSC for different modifications.

Sorbents	Modification	Oil type	$q_{max}(g/g)$	Improvement (%)	References
Corn stalk	Cellulase AC	Crude oil	24.98	402	This research
	Cellulase RC		16.3	223	
	AHP		14.08	183	
Corn stalk	Carbonization	Gasoline	8.7	130	[1]
Wheat straw	Autohydrolysis	Crude oil	6.9	72	[24]
Kapok	Acetylation	Diesel	36.7	20	[52]
Pomelo peel	Polymerization	Diesel	18.91	196	[53]
Kapok	Silanization	Engine oil	99.07	19	[54]

High regression coefficients (R^2) are observed for the pseudo-second-order kinetic model compared to the pseudo-first-order kinetic model and the intra-particle diffusion model. The results suggest that the sorption mechanisms using modified corn stalk mainly involved oil adhesion to the outer layer of the sorbent, and the chemisorption of oil onto the sorption sites of all sorbents through strong oil-sorbent interactions, equivalent to covalent bond formation or van der Waals forces [51].

3.4. Sorption isotherms

The experimental data were evaluated based on the Langmuir and Freundlich isotherm models, and all parameters are tabulated in Table 5, which can elucidate the sorption mechanisms. According to the correlation coefficients R^2 of ACCS, RCCS and AHCS, the sorption systems better fit the Langmuir model than the Freundlich model, which means both the enzymatically and chemically modified corn stalk had a homogeneous surface, on which oil molecules were sorbed in a monolayer. The maximum OSC was estimated, and the q_{max} values of all sorbents were in the order of ACCS > RCCS > AHCS, indicating that the corn stalk modified by cellulase had a higher oil sorption than the AHP-treatment corn stalk. All R_L values evaluated by Eq. (8) were between 0 and 1, implying that oil sorption by the modified corn stalk is favorable [36].

The Freundlich constants n and K_f represent the sorption intensity between the oil and sorbent. The affinity of the sorbent towards oil increases in proportion to the K_f values, shown by the maximum sorption of ACCS, which had the highest K_f value of 5.157. The values of n were all above 1, which indicated the favorability of sorption, and this conclusion agreed well with the Langmuir isotherm models.

It is noteworthy that the upgrade ratio of sorption capacities for modified corn stalks in this work was much higher than those in previous studies (Table 6). Compared to other modification methods, both the enzymatic and chemical methods utilized in this research significantly improved the oil sorption, which demonstrated that using AC, RC and AHP as modifiers is an efficient way to functionalize PBW to remove spilled oil.

3.5. Sorption mechanism

To elucidate the mechanism of oil sorption by modified corn stalk, BET, XRD and SEM were utilized to reveal the sorbent surface properties. The results indicate that the modification of corn stalk using both cellulase and AHP is mainly achieved by diversifying the corn stalk morphology, increasing the specific surface area and decreasing the crystallinity

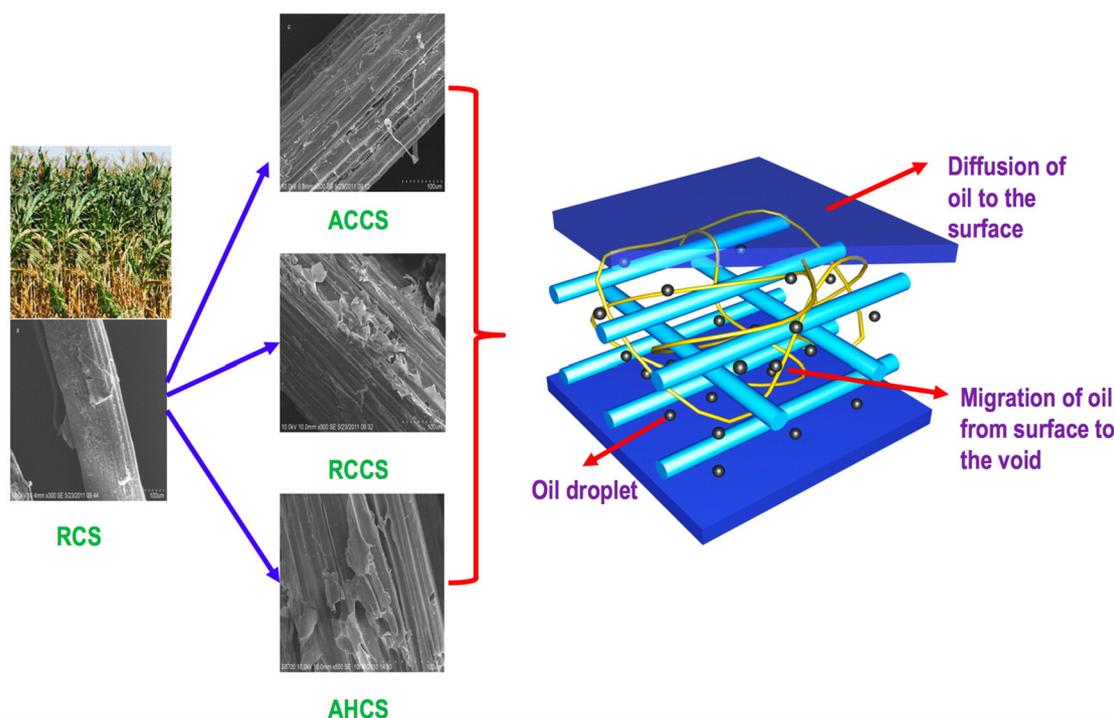


Fig. 5. Mechanism of oil sorption onto modified corn stalk.

of the cellulose fraction. With these changes, interactions between the corn stalk and the oil molecules and mechanical bonding are improved, and the oil molecules can easily penetrate the corn stalk, increasing the sorption capacity.

Based on this study, the method of oil sorption by ACCS, RCCS and ANCS was found to be chemisorption and monolayer sorption. The intra-particle diffusion of oil occurred during the entire sorption process, but the intra-particle diffusion was not the domination mechanism. The oil sorption mechanism could be concluded to include the following steps:

- > Diffusion of oil from the major body of solution to the surface of the sorbents
- > Migration of oil from the surface to the voids between and within the sorbents
- > Sorption of oil on the surface of the modified corn stalk, which may be due to the formation of pores and hollow tubules on the corn stalk surface, as shown in Fig. 5.

4. Conclusions

Oil sorbents made from corn stalk modified by cellulase and alkaline hydrogen peroxide were prepared. The results indicated that both treatment methods had notable effects on the modification to improve the OSC, and the effects of cellulase were more significant than those of AHP. All sorbents were better fit by the pseudo-second-order kinetic and the Langmuir isotherm model. Monolayer sorption on the surface and intra-particle sorption may lead to an increase in oil sorption. This work demonstrates that PBW modified by cellulase and AHP is a good biosorbents to recover spilled oil, which can solve the energy crisis and also handle the disposal of solid waste.

Acknowledgements

This research was financed by the Shenzhen Science & Technology Project (JCYJ20150417094158012 and JCYJ20160415114215737), and the China National Science Fund Program (51508206). The authors are

very grateful to Dr. Ashley Hill, department of biochemistry and molecular biology, Pennsylvania state university, for her efforts on the manuscript.

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