

Corn cob modified by lauric acid and ethanediol for emulsified oil adsorption

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Abstract: Corn cob is a naturally renewable material with developed micropore and hydrophobic characteristics, which enables it to show good oil adsorption capacity. In order to improve oil adsorption capacity, corn cob was modified with lauric acid and ethanediol. The structure of raw and modified corn cob was investigated using Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET) method, thermogravimetric analysis (TGA) and ZeTa potential analyzer. The effects of pH level, adsorption time, adsorbent dosage, and initial oil concentration on oil absorbency of corn cob were studied. The results indicate that the modification significantly improved the lipophilicity of corn cob, making the modified corn cob with much better adsorption capacity on oil absorbency. Compared with raw corn cob, the maximum saturated adsorption capacity of modified corn cob is 16.52 mg/g at pH 5, and the increasing percentage is found to be 141%, which indicates that the modification causes a better adsorption capacity for oil removal. In addition, due to high oil adsorption capacity, affordable price and low secondary pollution, the modified corn cob could be considered promising alternative for the traditional oil adsorbent to clean up the emulsified oily water.

Key words: emulsified oil; corn cob; lauric acid; ethanediol; lipophilicity

1 Introduction

Oil is widely used in our daily life as a major resource for the energy, food, and chemical industries. However, oil causes pollution during the various stages of its production, transportation, and utilization [1]. In recent years, recognition that oily wastewater needs to be removed has grown to protect water resources because oil pollution has adverse effects on the environment, living organisms and economy [2]. Water pollution from various types of oils continues to be a specific and serious problem. Oils found in outer drainage include edible oil, grease, kerosene, lubricants, diesel fuel, gasoline, and petroleum. These pollutants not only indicate the loss of oil but also have detrimental effects on the environment. And nowadays, many researchers have presented a lot of methods to treat with oily water.

Among the existing physical, chemical, and biological methods, adsorption is the most commonly used method for removing oils from water because of its low cost, simple design, and easy to conduct [3]. Several types of absorbents used to remove oily contaminants from water have been investigated. These absorbents include organic sorbents, such as activated carbon, sawdust, straw, hydrophobic aquatic plants, butyl rubber, and other carbon-based products; inorganic sorbents,

such as kieselguhr, organoclay, bentonite, and vermiculite and synthetic sorbents, including polyvinyl chloride, polyurethane, and nylon fibers [4]. Among these various materials, only synthetic fiber, which is also the most popular adsorbent, has been widely and successfully used. However, synthetic fibers have several disadvantages, including non-biodegradable, high cost, slow kinetics and limited removal capacity [5]. Thus, the search for the better oil adsorption materials with high uptake capacity, high adsorption rate, and affordable price is still ongoing [6].

Agricultural products have different uses, but most of them are generally treated as agricultural waste which it is necessary to burn [7]. Unfortunately, this option does not contribute to a better environmentally friendly world. Finding fields in which it may possible to use agricultural products can help to solve this problem and also deal with other things, such as the severe oily water pollution nowadays. Fortunately, many agricultural products have good oil absorbency including rice straw, peat moss, cotton, cotton grass, barks, milkweed, kenaf, and kapok [8]. These agricultural products exist in fibrous form that can be easily formed and conveniently applied. And obviously, some of them have the advantages over traditional oil absorbents: low cost, biodegradability, intrinsic hydrophobic characteristic and high sorption capacity [9–13].

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Among these agricultural products, because of wide plant area, large production and intrinsic porous nature, corn cob has a natural advantage to be a kind of absorbent.

Corn cob is a polyporous plant fiber derived from corn. Corn trees of family are cultivated in North Asia, Africa and most of Latin America. The corn cob fiber is polyporous, lightweight, non-allergic, non-toxic, biodegradable and odorless [14]. In recent years, corn cob has received increasing attention to be an oil sorbent because of developed pores and good buoyancy performance. In this work, corn cob was modified by using lauric acid and ethanediol in succession, taking esterification reaction in order to improve the lipophilicity of corn cob, the ability of corn cob in absorbing oil from water was evaluated, and the role of surface functional groups on the adsorption characteristics of the material as investigated.

2 Experimental

2.1 Materials

Corn cobs were collected from a farm in Hebei Province, China. Crude oil was obtained from Shengli Oil Field in Shandong Province, China. Sodium dodecyl benzene sulfonate (chemically pure), ethanediol (analytical grade) and lauric acid (analytical grade) were provided by Beijing Chemical Reagent Factory, China.

2.2 Preparation process

Faint yellow-colored raw corn cobs were cut into small pieces to obtain suitably sized corn cobs (4 mm to 10 mm). The pieces were washed with deionized water to remove any adhering substances and then oven-dried at 70 °C for 6 h. The pieces obtained were used as raw corn cob (RC) as shown in Fig. 1(a).

Treated RC was prepared using 10 g RC in 100 mL of pure lauric acid liquid. The mixture was allowed to

stand for 6 h at 70 °C and then filtered dry. The resultant adsorbent sample was then placed with a mixed solution (0.5 mol/L lauric acid ethanediol solution which had being reacted for 2 h at 70 °C) for 4 h at 70 °C, which yielded the end product referred to the modified corn cob (MC) as shown in Fig. 1(b).

Emulsified oily wastewater was prepared using a homogenizer operated at 2000 r/min for 2 h by mixing crude oil with deionized water after adding a certain amount of emulgator (sodium dodecyl benzene sulfonate). The amount of sodium dodecyl sulfate in the mixture was 4% by mass. The emulsion formed had been found stable for at least 24 h without noticeable phase separation under quiescent condition.

2.3 Oil concentration measurement

A specific amount of MC was mixed with a specific volume of emulsified oily wastewater while vibrating at 180 r/min for a certain period. Oleophilic long alkyl chain could be found on the surface of adsorbent adsorbed oil droplets, and then the dissociative oil droplets adhered to the adsorbed oil droplets, thereby reducing the oil concentration in the water sample. Figure 1(c) shows the process.

In this experiment, a 5 mL water sample was placed in a separating funnel, and then 3 mL 1:1 hydrochloric acid and a few drops of petroleum ether were added to the separating funnel and shaken for 3 min. The mixture was then allowed to stand for 3 min to make the two immiscible phases to separate. The quantity of oil transferred to the petroleum ether phase was removed to the colorimetric tube. The same steps were repeated three times. In the end, the petroleum ether was added to colorimetric tube line [15].

Oil concentration was measured based on the following equation:

$$C_w = C_0 \frac{V_w}{V} \quad (1)$$

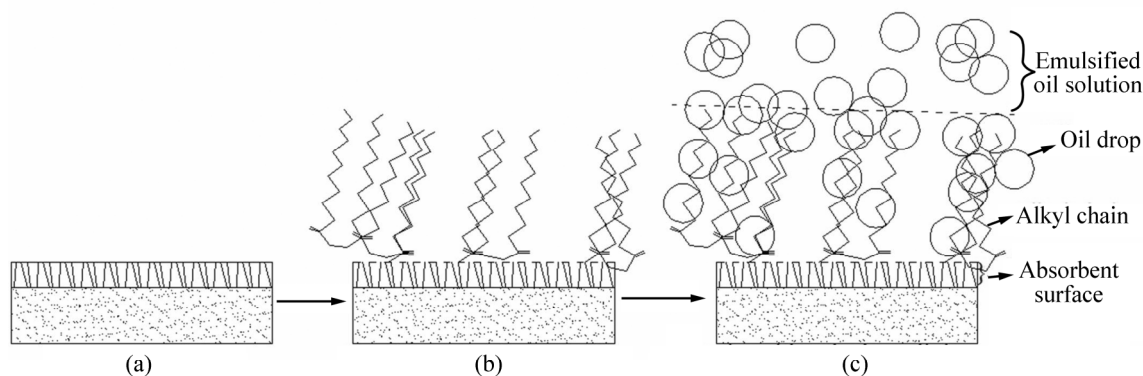


Fig. 1 Process of modification and oil adsorption of corn cob: (a) Raw corn cob; (b) Lauric acid and ethanediol modified corn cob; (c) Lauric acid and ethanediol modified corn cob after oil adsorption

where C_0 (mg/L) and C_w (mg/L) are the oil mass concentrations of colorimetric tube and water sample, respectively; V_w (L) and V (L) are the volume of colorimetric tube and the volume of water sample, respectively.

Oil mass concentration was determined using a ultraviolet spectrophotometer at 430 nm.

At any time, t , the adsorption uptake of oil adsorbed (q_t , mg/g) on absorbent was calculated using the following mass-balance equation:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (2)$$

where C_0 (mg/L) and C_t (mg/L) are the oil mass concentrations at initial time and time t , respectively; V (L) is the volume of water sample and m (g) is the mass of absorbent used.

2.4 Characterization of adsorbent

Functional groups were characterized using a Magna-750 Fourier transform infrared spectrometer using KBr pellets. Morphology identification was characterized using a Zeiss Evo18 scanning electron microscope. The BET was measured at 77 K using surface area and porosimetry analyzer, prior to measurement, the sample was given pretreatment by heating and vacuuming. The thermal analysis measurements were carried out on a NETZSCH STA 449F3 apparatus by increasing temperature from ambient to 923 K; the measurements were performed in dry air atmosphere, at a heating rate of 10 K/min. Charge characteristics were characterized using a Brookhaven Instruments Corporation zeta potential analyzer.

3 Results and discussion

3.1 Characterization fractions of corn cob fiber

3.1.1 Identification of functional groups

The description of the chemical structure of RC before and after modification, as well as before and after oil adsorption, could verify the possible functional groups involved in its binding mechanism. Figure 2 presents the FTIR spectra of RC, MC, and MC after oil adsorption.

Figure 2(a) shows a strong band at 3426 cm^{-1} , which could be attributed to the intra- and inter-molecular hydrogen-bonded (O—H) stretchings that occurred in cellulose and hemicellulose [16]. The peak observed at 2923 cm^{-1} could be assigned to the presence of C—H asymmetric stretching of $-\text{CH}_3$ groups. The presence of a peak observed at 1631 cm^{-1} could be attributed to the C=C stretching of aromatics. The broad peak at approximately 1050 cm^{-1} indicated the C—O stretching vibration of cellulose and hemicellulose [17].

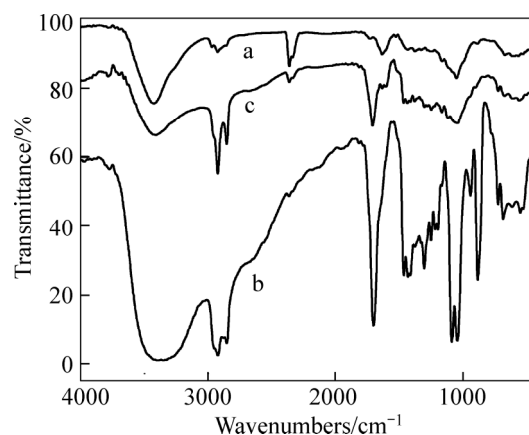


Fig. 2 FTIR spectra: (a) Raw corn cob (RC); (b) Modified corn cob (MC); (c) MC after oil adsorption

Figure 2(b) shows the increase in peak intensity of $-\text{CH}_3$ and $-\text{CH}_2$ groups after lauric acid and ethanediol modification, which demonstrated the successful chaining of the oleophilic long alkyl chains on the surface of the corn cob. This phenomenon was confirmed by the presence of the stronger peaks at 2920 cm^{-1} and 2850 cm^{-1} , which corresponded respectively to the $-\text{CH}_3$ and CH_2 groups originating from the lauric acid alkyl chain. The presence of new peaks at 3400 cm^{-1} and 1700 cm^{-1} indicated that the carbonyl group formed as a result of esterification reaction. In addition, the broad peak at approximately 1050 cm^{-1} became stronger, which indicated C—O stretching vibration of links between the long alkyl chain and cellulose and hemicellulose. These results were in a good agreement with the improvement in oil adsorption capacity of the corn cob from 6.86 mg/g to 16.52 mg/g after modification. The results further indicated that the increase of the lipophilicity of MC caused an improvement in its affinity with emulsified oil.

Figure 2(c) shows that the presence of a sharper peak at 3400 cm^{-1} indicated the attachment of emulsified oil. The well-pronounced sharp peaks at 2920 cm^{-1} and 1850 cm^{-1} were associated with $-\text{CH}_3$ and $-\text{CH}_2$ from emulsified oil, respectively. C=O stretching vibration at 1700 cm^{-1} and 1050 cm^{-1} decreased in intensity after oil adsorption, possibly because of the adsorption of emulsified oil and the presence of a covering oil layer.

3.1.2 Morphology analysis

Surface roughness with suitable porous structure could affect the oil adsorption capacity of natural fiber. Figure 3 shows the surface morphologies of raw and modified corn cobs. It can be seen that the surface morphologies have changed a lot after treatments. And the pore structures of RC and MC are also analyzed. The BET surface area and the volume of several types of pores (micropore volume, mesoporous volume and macroporous volume) were obtained as listed in Table 1.

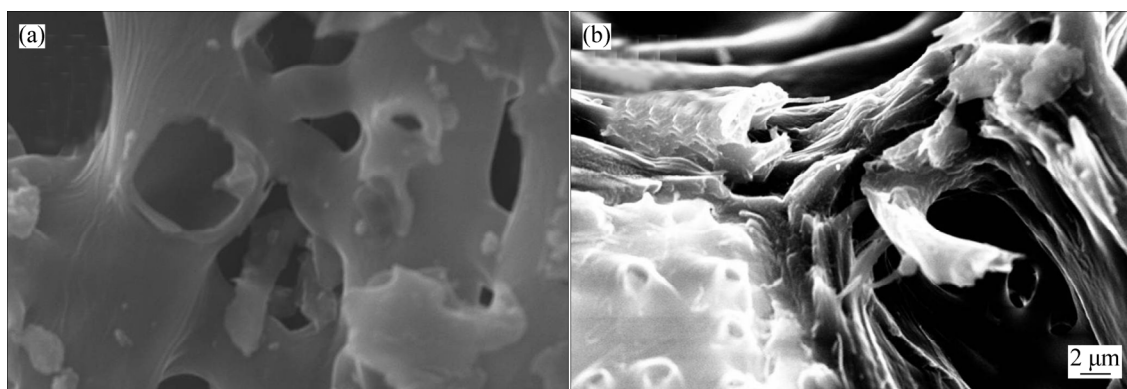


Fig. 3 SEM images of raw corn cob (a) and modified corn cob (b)

Table 1 Pore characteristics of raw corn cob (RC) and modified corn cob (MC)

Sample	BET surface area/ ($\text{m}^2 \cdot \text{g}^{-1}$)	Total pore volume/ ($\text{cm}^3 \cdot \text{g}^{-1}$)	Micropore volume/ ($\text{cm}^3 \cdot \text{g}^{-1}$)	Mesoporous volume/ ($\text{cm}^3 \cdot \text{g}^{-1}$)	Macroporous volume/($\text{cm}^3 \cdot \text{g}^{-1}$)
RC	87.4	0.0741	0.0476	0.0203	0.0062
MC	131.3	0.1561	0.1017	0.0413	0.0131

As shown in Fig. 3(a), raw corn cob is characterized by the developed void space structure, and surface area and pore volume from Table 1 also indicate that corn cob has a natural advantage to be a kind of adsorbent. Then, the modification by lauric acid and ethanediol was taken on corn cob in Fig. 3(b), in which corn cob became corroded and coarse with a layer of sticky substances, which improved surface area and pore volume. The formation of oleophobic alkyl chain did come from esterification reaction. In Table 1, the BET surface area and the total pore volume for MC increased, especially it had a distinct improve for micropore volume which had more than 65% of total volume. Thus, it had a noticeable consideration that the added oleophobic alkyl chain was perpendicular to the surface of corn cob, improving the BET surface area and the total volume. Therefore, due to bigger contact space between adsorbent and adsorbate, it made oil droplets easier to be adsorbed and gathered, then turning out a big advantage for MC to deal with oily water.

3.1.3 Charge characteristics

The zeta potentials of corn cob before and after the modification with lauric acid and also after the further treatment with ethanediol are shown in Fig. 4. It could be seen that corn cob carried negative electricity at various pH values no matter in the untreated situation or after the modification by lauric acid and ethanediol in succession. However, the electronegativity of corn cob became lower after the modification with lauric acid, and further weakened after the further modification with ethanediol. As lauric acid was a kind of fatty acid organic substance, the esterification reaction between corn cob and lauric acid reduced the amount of hydroxyl, and further ethanediol decreases the amount of carboxyl. Since oil

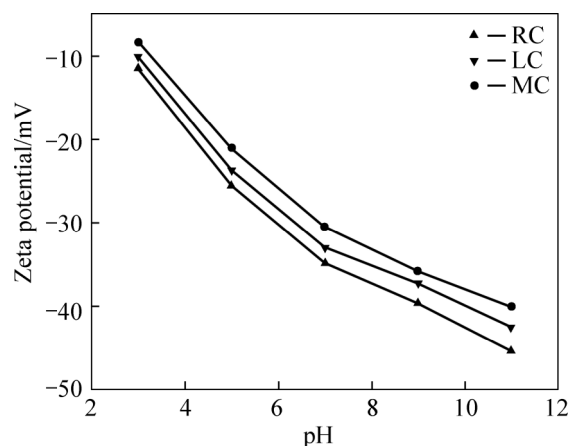


Fig. 4 Zeta potential of raw corn cob (RC), lauric acid modified corn cob (LC) and modified corn cob (MC)

droplets carried negative electricity, high electronegativity on the surface of raw corn cob made it hard to contact with oil droplets [18]. Obviously, with the consumption of hydroxyl and carboxyl and adding hydrophobic alkyl chains on the surface of corn cob, it turned easier for oil droplets to be adhered and gathered into a rounded mass by the as-prepared sorbent. And a higher lipophilicity could get a better oil-removing effects due to weaker lipophilicity. Compared with RC, MC showed an improved result, in which the method modified by lauric acid and ethanediol was confirmed and the changes of charge characteristics gave this kind of material a potential advantage to be an adsorbent.

3.1.4 Thermogravimetric analysis

The TG and DTG analyses of RC and MC are shown in Fig. 5. Obviously, the thermal decomposition of corn cob carries out on three stages: Firstly, in the temperature ranging from 25 °C to 130 °C, a little mass

loss in TG curve and a small peak in DTG curve involve the loss of moisture [19]; Secondly, the significant mass loss takes place at 150–500 °C due to the degradation of corn cob and distillation of oleophilic materials; Finally, no noteworthy mass loss was observed above 550 °C. As shown in Figs. 5(a) and (b), the intensity of peak in DTG curve was almost the same ranging from 25 °C to 130 °C owing to the presence of bound water [20]. However, an entirely different situation occurred between Figs. 5(a) and (b) at 150–500 °C. For Fig. 5(a), the main thermal decomposition occurred because of intrinsic hemicellulose, cellulose and lignin on corn cob in which the pyrolysis temperature of hemicellulose was 200–280 °C, cellulose 280–380 °C and lignin 380–500 °C [21]. As the modification changed the ingredients of the material, the DTG curve had three strange peaks ranging from 150 °C to 500 °C. The first significant mass loss taking place at 150–250 °C suggested the presence of oleophilic alkyl chain [22]. The second huge mass loss occurred at 250–350 °C ascribing to residual cellulose. The third little mass loss took place at 450–500 °C owing to the presence of residual lignin. However, compared with RC, the second and third mass losses on DTG curve of MC turned lower because of the depletion of hemicellulose, cellulose and lignin after the modification.

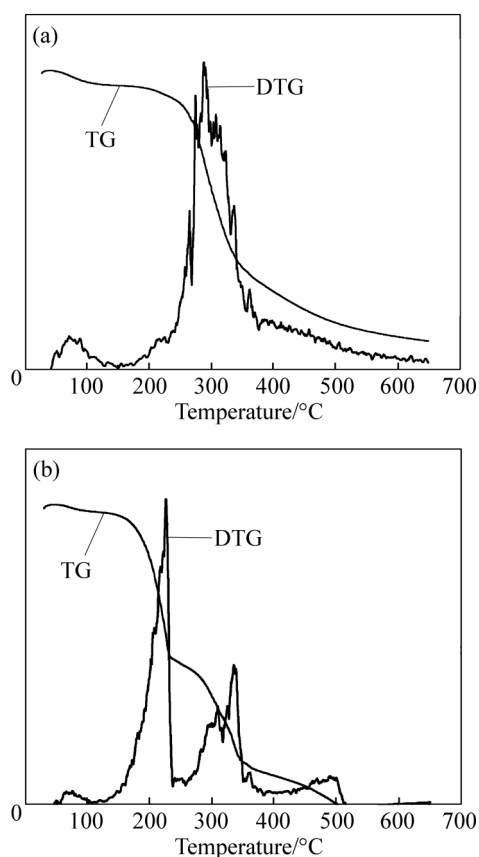


Fig. 5 TG and DTG curves of raw corn cob (RC) (a) and modified corn cob (MC) (b)

3.2 Test fractions of oil absorbency

3.2.1 Effect of initial concentration and pH

Figure 6(a) indicates the saturated oil adsorption capacity at various initial mass concentrations and pH. As the initial mass concentration increased, the adsorption capacity of the absorbent also increased at various pH levels until finally becoming balanced. Chances for collision between the absorbent and oil droplets likewise increased, which, similar to the bonding opportunity, resulted in a huge improvement in the saturated oil adsorption capacity of the absorbent. However, when the initial mass concentration went a further step, no further improvement on saturated oil adsorption capacity was observed. These results indicated that the amount of binding sites of absorbent to adsorb oil droplets was fixed in spite of the improvement of bonding opportunity [23].

At the same initial mass concentration, the saturated oil adsorption capacity at pH 5 was the maximum, whereas pH 9 was the minimum. Given that oil droplets carried the negative electricity, when the system was in weak acid, acidity could neutralize the negative

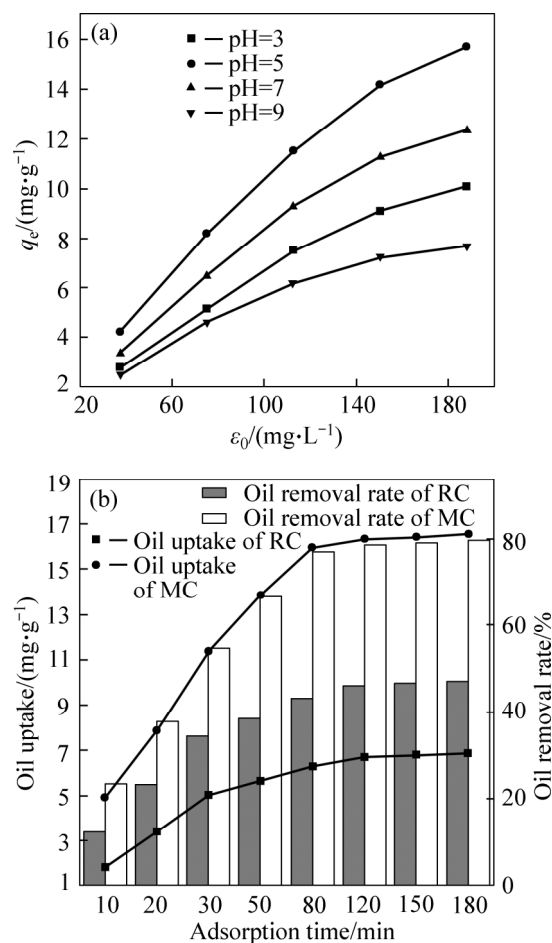


Fig. 6 Saturated oil adsorption capacity of modified corn cob (MC) at various original mass concentrations and pH (a), and effect of contact time of oil adsorption capacity and removal rate of raw corn cob(RC) and modified corn cob(MC) (b)

electricity of the emulsified oil system, destabilize the oil particles, thus improving the adsorption rate. As system acidity increased further, the saturated oil adsorption capacity of the absorbent decreased. One reason is that the ester group on the absorbent became unstable as a result of hydrolyzation, and the other is that as the acidity of the system improved further, the balance charge of the system would be broken and the extra acidity would cause the charge of the system to change from negative to positive, thereby emulsifying again and improving system stability. These two aspects reduced the effect of oil on the absorbent as acidity of the system improved further. When alkalinity of the system improved, the ester group would hydrolyze more easily, thereby reducing the hydrophobicity of the absorbent. Alkalinity would also cause the system more stable and the degree of emulsification would increase, which would consequently reduce the saturated oil adsorption capacity of the absorbent in an alkalinity system [24].

3.2.2 Effect of adsorption time

Figure 6(b) shows that the emulsified oil uptake of RC was rapid in the first 30 min, and for MC it was 80 min. Thereafter, both proceeded at a slower rate until finally attaining saturation. The initial high rate of the emulsified oil uptake of RC might be attributed to the bare surface of the developed aperture, which for MC could mean the oleophilic long alkyl chain due to the modification, resulting in an increase of oil adsorption sites [25]. As time was prolonged from 30 min to 80 min, the adsorption uptake of RC slowly increased, whereas for MC the time lasted from 80 min to 120 min. This result could be caused by the de-emulsification of oil droplets that could adhere to adsorbed oil droplets, which in turn caused a larger interfacial area for the adsorption to occur. For RC and MC, after 80 min and 120 min, respectively, the adsorption rate remained constant with time, presumably because of the saturation of RC and MC surfaces with emulsified oil particles as well as the equilibrium between adsorption and desorption processes that occurred after saturation. However, experimental data were measured at 180 min to ensure that full equilibrium was attained. The results indicate that almost 80 min for RC and 120 min for MC were required for the adsorption to start at a slow rate until the changes in adsorption uptake could be negligible relative to the contact time needed. Therefore, under this effect of contact time, we chose 80 min for RC and 120 min for MC as the optimum adsorption time to be used in further studies.

A comparison of RC and MC showed that the emulsified oil uptake had a significant improvement after modification from 6.86 mg/g of oil uptake for RC to 16.52 mg/g of emulsified oil uptake for MC. After modification, the corn cob was covered by a layer of

nonpolar substances and its additional lipophilicity improved the adsorption rate and adsorption capacity [26].

3.2.3 Adsorption dynamics

The rate of adsorption of emulsified oil by adsorbent was determined using three simple kinetic analyses shown in Figs. 7 and 8. The first is pseudo-first-order kinetic model, which is expressed by

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

where q_e (mg/g) and q_t (mg/g) are the amounts of adsorbate adsorbed at equilibrium and at any time t (min), respectively; k_1 (g/(mg·min)) is the adsorption rate constant of pseudo-first-order kinetic model.

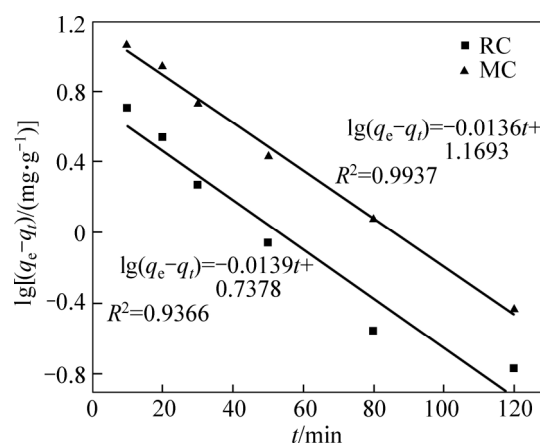


Fig. 7 Pseudo-first-order adsorption dynamic equation of raw corn cob (RC) and modified corn cob (MC)

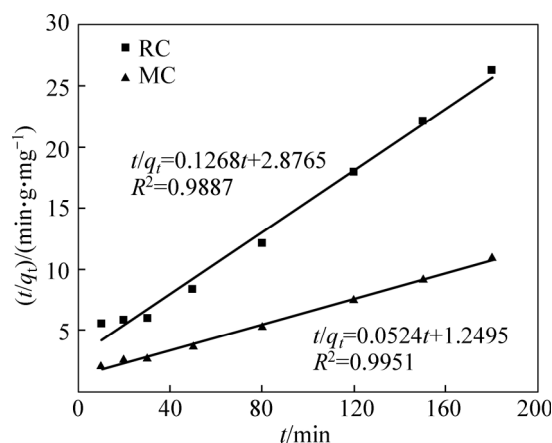


Fig. 8 Pseudo-second-order adsorption dynamic equation of raw corn cob (RC) and modified corn cob (MC)

The pseudo-second-order kinetic model is based on adsorption equilibrium capacity and expressed as

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

where q_e (mg/g) and q_t (mg/g) are the amounts of adsorbate adsorbed at equilibrium and at any time t (min),

respectively; k_2 (g/(mg·min)) refers to the adsorption rate constant of pseudo-second-order kinetic model.

The Weber and Morris model is used to characterize the diffusion in the granules and expressed as

$$q_t = k_a t^{1/2} \quad (5)$$

where q_t (mg/g) refers to the amount of adsorbent adsorbed at any time t (min); k_3 (g/(mg·min^{1/2})) refers to the adsorption rate constant of the Weber and Morris model.

Table 2 indicates that the correlation coefficients (R^2) for the first-order reaction of RC and MC were both lower than 1.0 (i.e., 0.9366 and 0.9937), respectively. For the pseudo-second-order equation, a two-step linear relationship was obtained, and the R^2 values for the reactions of RC and MC were 0.9887 and 0.9951, respectively. The result suggested that the adsorption of emulsified oil by RC and MC was not of the first-order. It was fitted better with the second-order based on the adsorption capacity, predicting the behavior over the entire range of studies supporting validity, and in agreement with multilayer adsorption being the rate-controlling process. For RC, adsorption capacity was mainly controlled by a paraffin wax layer and developed apertures on the surface of RC, whereas for MC, adsorption capacity was mainly controlled by oleophilic long alkyl chains. The slope showed the rate of chemical adsorption of MC was fairly quicker than that of RC.

For the Weber and Morris models of RC and MC, Fig. 9 indicates that both RC and MC had two adsorption phases: the first stage, which involved rapid adsorption controlled by surface diffusion, and the second stage, which involved slow adsorption controlled by intraparticle diffusion [27]. A comparison of the rates of adsorption of RC and MC showed that at the first stage, the adsorption rate of MC was twice over RC. The adsorption of surface diffusion of MC was faster because of the additional oleophilic long alkyl chain formed from modification, which could easily catch oil droplets and be further adsorbed by micro pores. The well-developed oleophilic long alkyl chain and micro pores allowed it to easily form an attractive field to improve the oil uptake. In the second stage, the rate of adsorption for both RC and MC was extremely slow and utilized mainly surface

adsorption of the corn cob. However, the rate of MC was significantly faster than RC because of the formed intricate oleophilic long alkyl chain and much more developed micro pores of MC.

3.2.4 Adsorption isotherms

The Langmuir and Freundlich isotherms were used to analyze the adsorption isotherm results as shown in Figs. 10 and 11.

The Langmuir isotherm is expressed as

$$\frac{C_e}{q_e} = \frac{1}{Q_0 K_L} + \frac{1}{Q_0} C_e \quad (6)$$

where q_e (mg/g) is the saturated oil adsorption corresponding to complete monolayer coverage and K_L is the Langmuir constant.

The Freundlich isotherm is expressed as

$$\lg q_e = \lg K_f + \frac{1}{n} \lg C_e \quad (7)$$

where q_e is the saturated oil adsorption at equilibrium (mg/g); C_e is the liquid phase sorbate concentration at equilibrium (g/L); K_f is the Freundlich constant.

A comparison of the slope of curve and regression coefficient, R^2 , between the studied isotherms was conducted to determine the isotherm model best fitted to the experimental data as listed in Table 3. The plots for the Langmuir isotherm at various pH levels indicated good R^2 above 0.9. However, for the Freundlich isotherm, R^2 was above 0.9 only at pH=5; and others were all lower than 0.9. Thus, the isotherm model for adsorption of emulsified oil on MC could be best described by the Langmuir model. And on the surface of MC, it gave a large role for intrinsic wax layer and added oleophilic alkyl chain for oil droplets adsorption [28]. The process of adsorption might have involved four steps, including 1) contact between oleophilic long alkyl chain and oil droplets, 2) adsorption of oil droplets by oleophilic long alkyl chain and intrinsic wax layer, 3) diffusion of oil droplets into the micro pores, and 4) oil droplets coalescence on the surface of adsorbent. The first part of adsorption was extremely quick at the initial contact time, and at almost the same time. The second part began, which was influenced by the first part. And then the third part took place due to developed micro pores and big BET surface area. In the end, it formed slower for oil droplets coalescence. However, it had a large role in oil-removal.

Table 2 Slope and correlation coefficient of various adsorption dynamics of raw corn cob (RC) and modified corn cob (MC)

Parameter	Pseudo-first-order adsorption dynamics		Pseudo-second-order adsorption dynamics		Weber and Morris model			
					Rapid stage		Slow stage	
	RC	MC	RC	MC	RC	MC	RC	MC
k	-0.0139	-0.0136	0.1268	0.0524	1.3743	1.8424	0.2083	0.2691
R^2	0.9366	0.9937	0.9887	0.9951	0.9868	0.9236	0.7630	0.8920

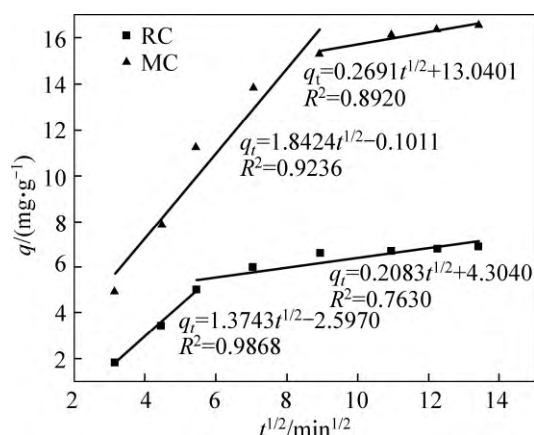


Fig. 9 Weber and Morris models of raw corn cob (RC) and modified corn cob (MC)

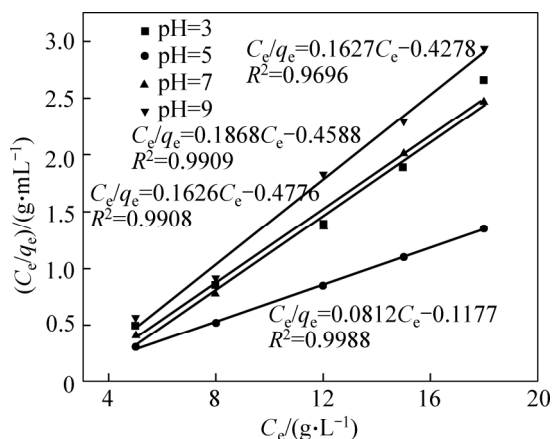


Fig. 10 Langmuir isotherm of emulsified oily water on modified corn cob (MC) at various pH values

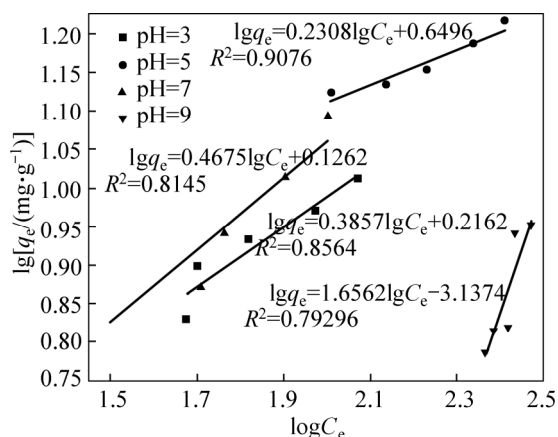


Fig. 11 Freundlich isotherm of emulsified oily water on modified corn cob (MC) at various pH values

3.2.5 Comparison of oil adsorption capacities from this work and other oil adsorbent fibers

Table 4 presents a comparison of the effectiveness of corn cob as a potential adsorbent for treatment of emulsified oily water in terms of the maximum adsorption capacity with other adsorbent fibers. Obviously, because of high hydrophobicity, the

Table 3 Slope and correlation coefficient of Langmuir and Freundlich isotherm of modified corn cob (MC)

pH	Langmuir isotherm		Freundlich isotherm	
	k	R^2	k	R^2
3	0.1627	0.9696	0.3857	0.8564
5	0.0587	0.9988	0.2308	0.9076
7	0.1626	0.9908	0.4675	0.8145
9	0.1868	0.9909	1.6562	0.7930

Table 4 Comparison of oil adsorption capacities from this work and other oil absorbing fibers

Sorbent	Adsorbate	Adsorption capacity/(g·g ⁻¹)	Ref.
Acetylated banana fiber	Oil spill	18.12	[9]
Porous polystyrene fibers	Diesel	7.13	[10]
Carbonized rice husk	Heavy oil	>6	[11]
Surfactant modified barely straw	Mineral oil	613.3×10 ⁻³	[12]
	Canola oil	584.2×10 ⁻³	
Walnut shell	Mineral oil	0.56	[13]
	Vegetable oil	0.58	
	DoAll Bright-Edge oil	0.74	
Raw corn cob	Crude oil	5.12	
	Emulsified oil	6.85×10 ⁻³	
Lauric acid and ethanediol modified corn cob	Crude oil	10.37	This work
	Emulsified oil	16.52×10 ⁻³	

acetylated banana fiber [9] gave a very high adsorption capacity compared with other adsorbents. Besides, many researches found that surface area played an important role in the improvement of oil adsorption capacity. So, when compared to carbonized rice husk [11] and porous polystyrene fibers [10], it was found that modified corn cob exhibits higher adsorption capacity when it treats with the similar oil. Taking the removal of mineral oil of surfactant modified barely straw [12] and walnut shell [13] as the point of reference, modified corn cob was found to exhibit lower adsorption capacity when dealing with the fairly stable oil, namely emulsified oil. Evidences show that some modification on adsorbents could enlarge micropores and enhance lipophilicity, simultaneously, and this kind of modification could make oil adsorption capacity of adsorbents a huge improvement. As corn cob gave a desired results to the treatment of crude oil and emulsified oil, it had a notable evidence for the successful modification on the surface of adsorbent.

4 Cost estimation

Nowadays, synthetic fibers play a dominant role in oily water cleanup, which are very expensive and available for approximately US \$ 80–120/kg. In spite of high oil adsorption capacity around 10 g/g, the cost of the materials is relatively high [29]. Besides, synthetic fibers also have some adverse factors: difficult to biodegrade and polluting environment, thus it has more attention on some simple and cheap materials. In this work, the raw material, corn cob, is derived from corn free of cost, as a waste, and considering the cost of transport, chemicals used for the surface modification, electrical energy, labor and processing wastes of as-prepared sorbent, the modified corn cob costs approximately US \$ 25/kg. Therefore, the modified corn cob could be considered an alternative to traditional synthetic materials due to high adsorption capacity, biodegradability and low cost.

5 Conclusions

The results of this work demonstrate that the oil sorption behavior of corn cob is enhanced significantly after the modification with lauric acid and ethanediol. The corn cob adding the hydrophobic long alkyl chains enhances its oleophilic property and improves its capacity to adsorb emulsified oil droplets. Adsorption of emulsified oil by biomass waste materials indicates a decrease in chemical oxygen demand, thereby making MC a better candidate than conventionally costly adsorbents. In the meantime, the use of corn cob has no environmental impact. Thus, lauric acid and ethanediol modified corn cob can be used as a potential sorbent in oily wastewater treatment.

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