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Oil Spill Cleanup using Stearic-acid-modified Natural Cotton

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Abstract

Natural cotton was chemically modified by stearic acid under different reaction conditions using 4-(dimethylamino) pyridine (DMAP) and *N, N'*-dicyclohexyl carbodiimide (DCC) as a catalyst and a co-catalyst, respectively. The structure of modified cotton was confirmed using Fourier transform infrared (FT-IR) measurement. The hydrophobicity of the modified cotton increased after modification, with water contact angles in the range of 141–144º. Scanning electron microscope (SEM) images of the cotton before and after modification were similar with fairly smooth surfaces. The modified cotton absorbed oils and organic solvent but not water due to the hydrophobicity of the cotton. The absorption capacities of the modified cotton were 23–26, 21–25, 20–24, and 29–32 times the cotton weight for crude oil, cooking oil, motor oil, and chloroform, respectively. The modified cotton could be reused many times without any loss of absorption capacity and could be used under different pH conditions.

Keywords: natural cotton, oil sorbent, modified cotton, hydrophobic cellulose, oil spill cleanup

Introduction

Crude oil is one of the most important energy sources for humans and is the major precursor for polymer and petrochemical synthesis. The exploration, production, transportation and storage of crude oil can cause oil spillage and leakage, although new technologies for these processes have been developed. Oil spillage has many negative effects on the environment and damages the biodiversity in the contaminated areas. Therefore, various methods and processes have been investigated to address the oil spill problem. There are several means of oil spill cleanup, such as using booms, dispersants, marine bacteria, and sorbent materials.

Sorbent materials with both oleophilic (oil-attracting) and hydrophobic (water-repellent) characteristics can be used as oil sorbents, and they are classified into three main categories: synthetic, natural inorganic and natural organic.[1–3] Synthetic sorbents are artificial polymeric materials such as polyurethane, polyethylene, and polypropylene.[4–8] These materials account for most of the commercial sorbents used for oil spill cleanup because of their hydrophobicity and oleophilicity.[1, 4–8] Natural inorganic sorbents, such as clay, perlite, vermiculite, glass wool, sand, and volcanic ash, can absorb oils up to 20 times their weights. Natural organic sorbents include peat moss, straw, sawdust, feathers, corncobs, cotton fibers, cellulosic kapok fibers, and other similar carbon-based products.[1, 2] They are mostly cellulose-based, environmentally friendly, degradable, and inexpensive materials. However, because of the hydroxyl groups on their structures, these materials are hydrophilic, limiting their application in oil spill cleanup. Therefore, hydrophobic modification is required for natural organic materials so that they can be used as oil sorbents.

Cellulosic materials can be hydrophobically modified physically or chemically. Cellulosic materials can be physically modified by cold-plasma, coating, and surface crystal growth treatments, among other methods.[9] For example, a cellulose aerogel surface can be treated with a CCl_4 cold plasma to become hydrophobic, with the water contact angle increasing to 102º. [9] A nanocellulose arogel was coated with TiO_2 to change its hydrophobicity.[9, 10] In addition, several methods have been investigated and reviewed in the literature for the chemical hydrophobic modification of cellulosic materials, such as grafting, sol-gel, and atom transfer radical polymerization (ATRP).[9] The grafting approach is the best-known method for chemically modifying cellulosic materials. The hydroxyl groups primarily responsible for cellulose's hygroscopicity could be replaced by hydrophobic groups in several ways.[10–12] For example, the acetylation of hydroxyl groups in rice straw was investigated using acetic anhydride with or without tertiary amine catalysts, resulting in a significant increase in the hydrophobicity.[11, 13] Another acetylation approach was carried out on banana fibers and sugarcane in the presence of an N-bromosuccinimide (NBS) catalyst.[14–16]

Fatty acids have also used to improve the hydrophobic and oleophilic characteristic of organic materials.[17–22] For instance, the oil absorption capacity of banana trunk fibers increased significantly after being modified by oleic and stearic acid using sulfuric acid as a catalyst.[19] A long-chain stearic anhydride was also used for the esterification of paper sheets at room temperature in the presence of pyridine as a catalyst to change the hydrophobicity of the paper sheets.[20] In this study, we prepared natural cottons chemically modified with stearic acid in the presence of 4-(dimethylamino) pyridine (DMAP) as a catalyst and *N*,*N*'-dicyclohexyl-carbodiimide (DCC) as a co-catalyst, and we used the prepared cotton samples for the removal of oils and organic solvent. The thus-obtained cottons were characterized using field emission scanning electron microscopy (FE-SEM) and Fourier transform infrared (FT-IR) spectroscopy. The oil absorption capacity and re-usability of the modified cottons were also investigated.

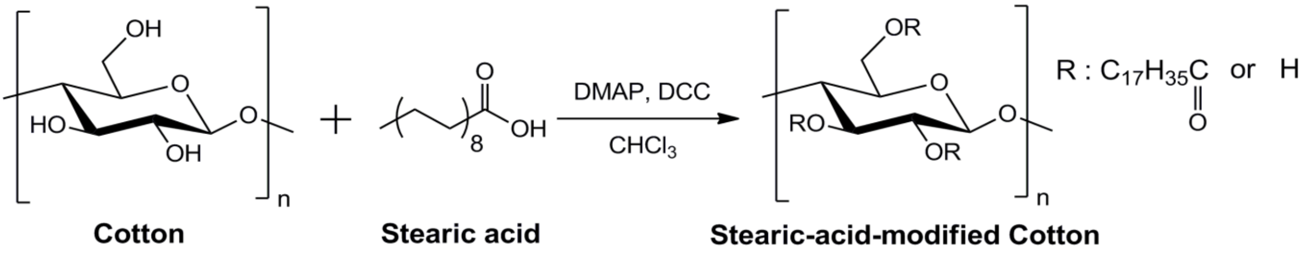
2. Materials and methods

2.1. Materials.

Natural cotton was supplied by Bach Tuyet Cotton Corp. (Vietnam). Stearic acid was purchased from Xilong Chemical (China). 4-(Dimethylamino) pyridine (DMAP) and *N*, *N'*-dicyclohexyl carbodiimide (DCC) were supplied by Sigma-Aldrich. Cooking oil was supplied by Tuong An Vegetable Oil JSC (Vietnam). Motor oil was purchased from Castrol Vietnam. Crude oil was received as a gift from Research and Engineering Institute (R&EI), Vietsovpetro JV (VSP). Acetone, ethanol, and chloroform were purchased from Xilong Chemical Co., Ltd.

2.2. Preparation of stearic acid modified cotton.

The modified cotton samples were prepared as follows. 0.4 g of commercial cotton was immersed into a 40 mL solution of stearic acid (0.4 g) and DCC (0.32 g) in $CHCl_3$ (Scheme 1). DMAP was then added to the thus-prepared mixtures in different amounts. The reaction was performed at different temperatures, as shown in Table 1. After the reaction, the modified cotton samples were washed three times using acetone and dried at 70 °C.



Scheme 1. Chemical modification of cotton using stearic acid.

2.3. Measurements.

Infrared spectra were measured using a Bio-Rad FTS-60A FT-IR spectrometer equipped with an MTC (mercury-cadmium-telluride) detector at a resolution of 2 cm^{-1}. The morphology of the material was examined using a field-emission scanning electron microscope (FE-SEM, JSM-6701F). The water contact angles (WCAs) of the cotton samples were measured using an optical contact angle meter (OCA, Data Physics) with 4μL water droplets. The oil absorption capacities of the cotton samples were measured by immersing the modified cottons into various organic solvents and oils for 30 min until they were saturated. The absorption capacity, *A*, was determined by the equation $A = (W_{saturated} - W_{initial})/W_{initial}$, where $W_{saturated}$ and $W_{initial}$ are the weights of the modified cotton before and after absorption.

3. Results and discussion

3.1. Preparation of stearic acid modified cottons

Pure cotton is a well-known porous material that can absorb both oil and water. Pure cotton must undergo hydrophobic modification before it can be used for the selective absorption of oil and organic solvents. Stearic acid, which is a typical water-repellent fatty acid, was used to hydrophobically modify cotton. A facile method of deep-coating was first tested by soaking pure cotton in solution of stearic acid at different concentrations in chloroform. The effects of the concentration of stearic acid on the loading percentage of stearic acid in cotton and on the WCA were investigated, and the results are shown in Figure 1. The loading percentage of stearic acid in the cotton linearly increased with an increasing stearic acid concentration. It was predicted that the hydrophobicity of the treated cotton would increase with an increasing stearic acid amount in the cotton. However, the WCA measurements shown in Figure 1 illustrated that the WCAs of the treated cottons were mostly unchanged, irrespective of the increasing loading percentage of stearic acid in the cotton. The WCA of the stearic acid-coated cotton was approximately 75º, which is still hydrophilic, so the thus-treated cotton could not be used as selective oil sorbent.

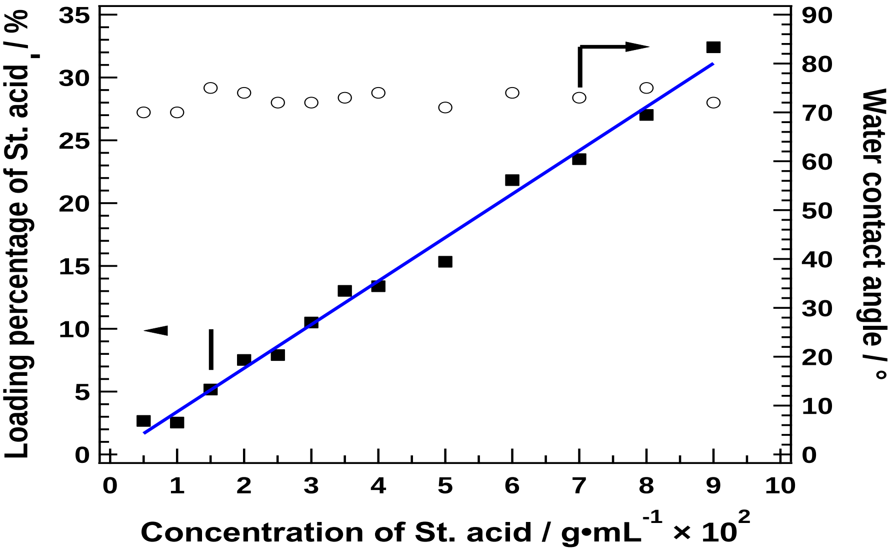


Figure 1. Effect of the stearic acid concentration on the loading percentage of stearic acid in the cotton and on the water contact angle of the stearic acid-treated cotton. St. acid denotes stearic acid.

The cotton samples were chemically modified by reacting with stearic acid at different conditions, as shown in Table 1. The chemical hydrophobic modification of cotton using stearic acid was confirmed using FT-IR, and the results are shown in Figure 2. The FT-IR spectra of pure cotton and modified cotton were broad and fairly similar except for the region of 1650–1800 cm^{-1}. A new broad peak appeared at 1750 cm^{-1} in the spectrum of the modified cotton, and this peak was assigned to the vibration of ester groups that could not be found in the spectrum of pure cotton. This result implied that stearic acid was successfully grafted onto the cotton by forming ester bonds with the hydroxyl groups on the cotton.

The WCA results of modified cotton are described in Table 1. The pure cotton without modification immediately absorbed water, so its WCA was approximately 0º. In contrast, all of the cotton samples after reacting with stearic acid showed WCAs over 140º. These results indicated that the hydrophobicity of cotton increased after being modified by stearic acid. The modification reactions were performed at different conditions to investigate the effect of the amount of DMAP catalyst and the effect of the temperature on the WCAs of the cotton samples. However, the results in Table 1 illustrate that the WCA of cotton seemed to be independent of the DMAP content and the temperature. The WCAs of the cotton samples could not reach 150º because the reactions occurred in a heterogeneous environment, limiting the reaction between the cotton and stearic acid.

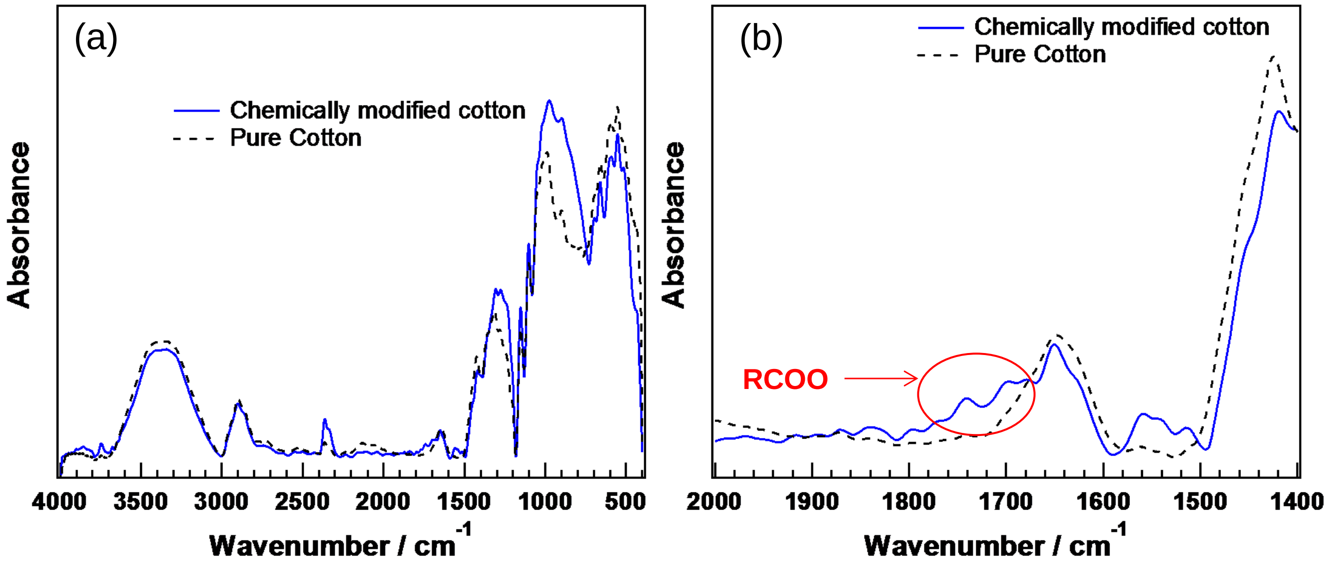


Figure 2. FT-IR spectra of pure cotton and cotton chemically modified by stearic acid. (a) region of 4000–400 cm^{-1}, (b) region of 2000–1400 cm^{-1}.

Table 1: Effect of reaction conditions on WCA and oil absorption capacity [a]

Run	% DMAP [b]	Temperature / °C	WCA / °	Oil absorption capacity (*A*) [c]			
				Crude oil	Cooking oil	Motor oil	Chloroform
1	0	50	0	–	–	–	–
2	3	50	141 ± 2	23 ± 2	22 ± 2	20 ± 2	31 ± 2
3	7	50	142 ± 1	24 ± 2	25 ± 2	22 ± 2	29 ± 2
4	12	50	144 ± 2	26 ± 2	22 ± 2	22 ± 2	30 ± 2
5	20	50	143 ± 2	25 ± 2	25 ± 2	22 ± 2	32 ± 2
6	7	0	144 ± 1	25 ± 2	21 ± 2	20 ± 2	29 ± 2
7	12	0	142 ± 2	24 ± 2	21 ± 2	24 ± 2	31 ± 2
8	7	30	144 ± 2	25 ± 2	22 ± 2	20 ± 2	30 ± 2
9	12	30	143 ± 1	26 ± 2	25 ± 2	23 ± 2	32 ± 2

[a] In $CHCl_3$, 0.4 g cotton, 0.4 g stearic acid, 0.32 g DCC. [b] $\%_{DMAP} = 100\% \bullet m_{DMAP}/m_{DCC}$. [c] $A = (W_{saturated} - W_{initial})/W_{initial}$, where $W_{saturated}$ and $W_{initial}$ are the weights of the modified cotton before and after absorption, respectively.

The morphologies of the cotton samples before and after modification were determined by FE-SEM and are shown in Figure 3. The SEM images illustrated that cotton fibers before and after modification by stearic acid had wired structures with fairly smooth surfaces. The unchanged morphologies of the cotton samples before and after reaction with stearic acid indicated that no stearic acid adsorbed on the surface of the cotton after modification. This result is in good agreement with FT-IR result, in which the vibrational peaks of stearic acid could not be detected in the spectrum of the modified cotton (Figure 2).

3.2. Oil absorption capacity and reusability

Natural cotton is a well-known sorbent material with a highly porous structure. It can absorb both oil and water. However, the selective absorption of oils or organic solvents of cotton is limited due to its intrinsic hydrophilicity. The hydrophobicity of cotton could be increased via reacting cotton with stearic acid to allow the use of cotton as an oil sorbent. The hydrophobicity and oleophilicity of the modified cottons were determined by WCA measurements and by spotting water and crude oil onto the cotton surface. Figure 4a clearly shows that colored water droplets stood on the surface of cotton with WCAs of more than 140º (inset in Figure 3d). In contrast, the crude oil was immediately absorbed into the modified cotton. These results indicated that cotton chemically modified by stearic acid was hydrophobic and oleophilic, so it could be utilized as a selective oil sorbent. The crude oil absorption process was studied by placing the modified cotton into a Petri dish containing crude oil floating on a water surface. The modified cotton immediately absorbed crude oil, but not water, and after 5 seconds, all of the crude oil in the Petri dish was absorbed into the modified cotton (Figure 4 c→f).

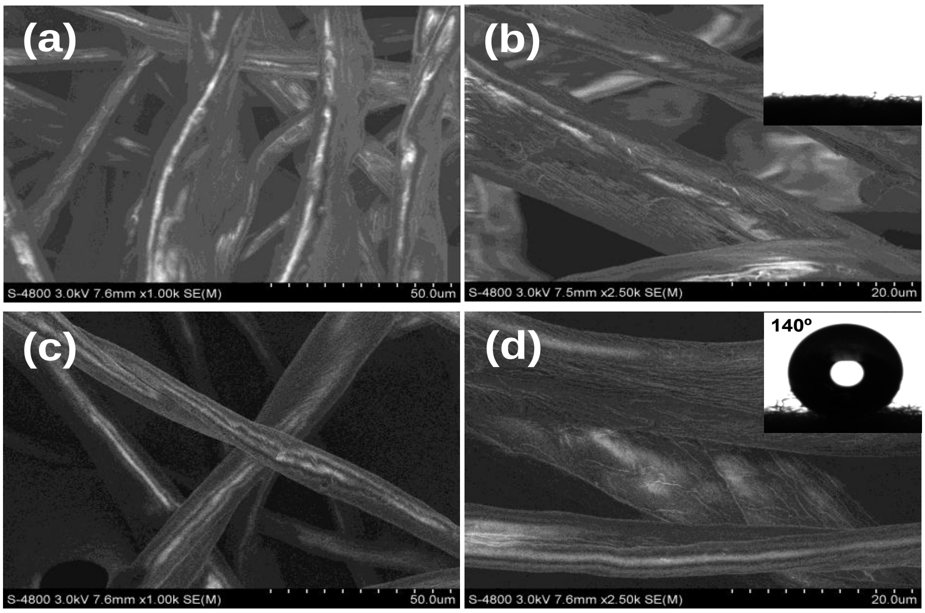


Figure 3. SEM images of (a), (b) pure cotton with magnifications of 1000x and 2500x, respectively, and (c), (d) stearic acid chemically modified cotton with magnifications of 1000x and 2500x, respectively. The insets in (b) and (d) are the water contact angle measurements for the pure cotton and the chemically modified cotton, respectively.

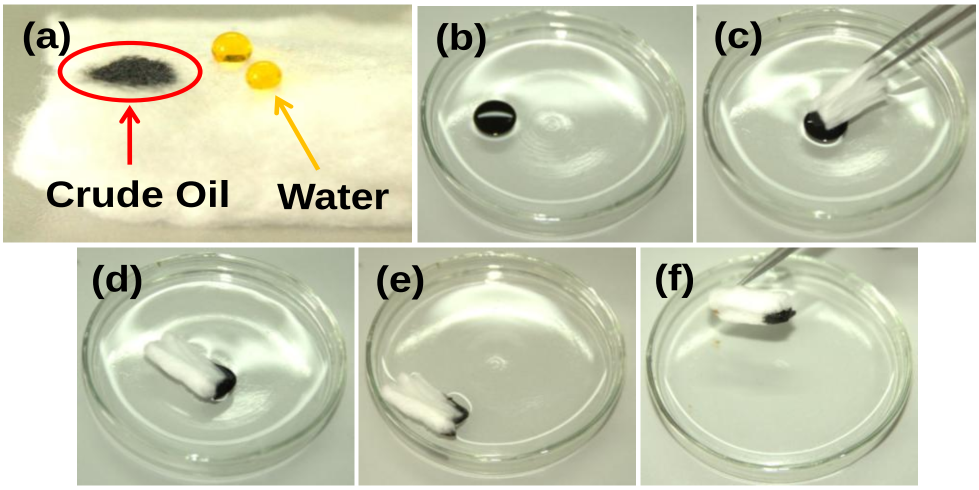


Figure 4. Snapshots of (a) crude oil and water (colored by methyl orange) spotted on the surface of the modified cotton, (b) crude oil on a water surface, and (c→f) the process of crude oil absorption by the chemically modified cotton.

The possibility of using modified cotton in different pH environments was confirmed by measuring the WCAs of modified cotton at pH 4, 7, and 10. The WCA was almost the same at the three above-mentioned pH values. In particular, at basic pH (pH 10), the WCA was 142° which is similar to those at pH 4 and 7. This result once again demonstrated that stearic acid did not adsorb on the surface of cotton, which would have resulted in stearic acid dissolving, and the WCA decreasing, at a basic pH.

The absorption capacity of the modified cotton was evaluated by absorption experiments. Typically, the modified cotton samples were immersed into various oils and organic solvents for 30 min until they were saturated. The absorption capacity of the modified cotton is shown in Table 1. The modified cottons could absorb crude oil, cooking oil, motor oil, and chloroform approximately 23–26, 21–25, 20–24, and 29–32 times their weights, respectively. The absorption capacities of modified cotton in this paper are comparable to those of previous studies. For example, rice straw after acetylation showed the absorption capacity for oils in the range of 16.8−24 times its weight.[7] Acetylation of sugar-cane bagasse and banana fiber exhibited the absorption capacity for oils in the range of 18.12−24 times its weight.[10-12]

The reusability of the modified cotton was studied by repeating absorption experiments followed by washing the absorbed cotton with ethanol and drying at 70 °C for 1 hour for each cycle. The result shown in Figure 5 implies that the modified cotton could be reused up to ten times without any loss of absorption capacity.

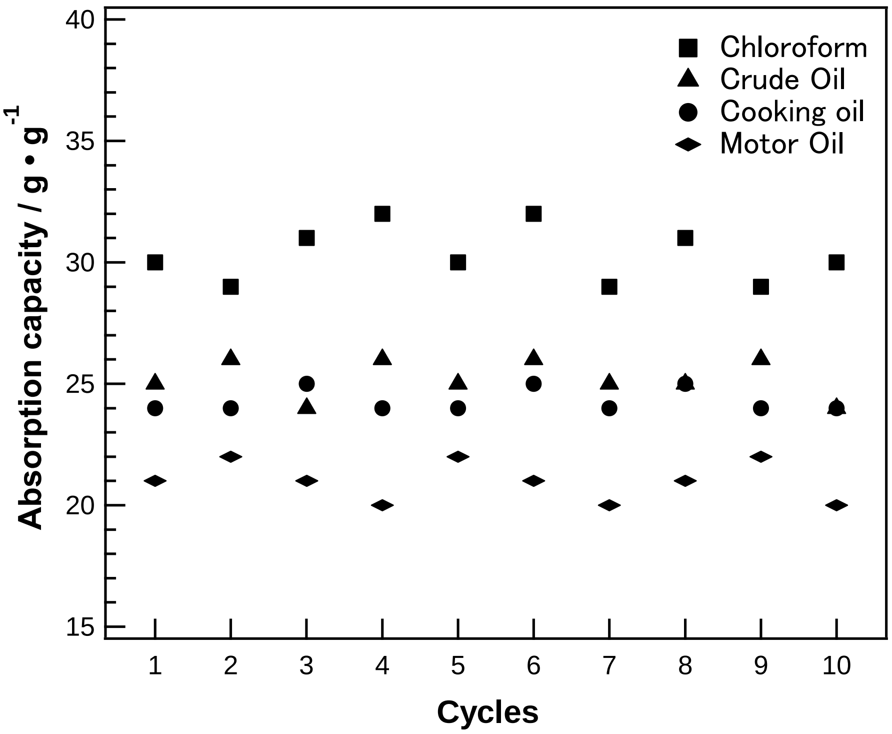


Figure 5. Reusability of the modified cotton for chloroform, crude oil, cooking oil and motor oil absorption.

Conclusion

Natural cotton sponges after modification by stearic acid in the presence of 4-(dimethylamino) pyridine and *N*, *N'*-dicyclohexyl carbodiimide were hydrophobic, with water contact angles in the range of 141–144°. The modified cotton samples could be applied as oil/organic solvent sorbents with absorption capacities in the range of 21–32 times their weights, depending on the types of oils and organic solvents. The absorption capacity of the modified cotton was mostly unchanged after using them up to ten times. The results implied that cotton modified by stearic acid could be a good candidate for an crude oil sorbent material.

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