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Thermodynamic studies of acetylated Hibiscus sabdariffa L. fibre for use as oil sorbents

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Abstract

The fibre of *Hibiscus sabdariffa Leaves* was modified through hydrophobic treatment with acetic anhydride in the presence of N-bromosuccinamide as catalyst at a temperature between 35 and 80^{0}C. The result shows a corresponding increase in the extent of acetylation of the fibre with increase in temperature and catalyst amount. The extent of acetylation was investigated using Fourier transform infrared spectroscopy (FTIR). Thermodynamic models enabled the evaluation of heat of acetylation, entropy change and the changes in Gibb's free energy of the acetylation process at the studied temperatures. The change in entropy (ΔS) was positive, ΔG was negative and the heat of acetylation was negative. The morphology of the fibre was studied using scanning electron microscopy (SEM).

1. Introduction

When there is an oil spill on water, spreading immediately takes place. The gaseous and liquid components evaporate. Some get dissolved in water and even oxidize, and yet some undergo bacterial changes and eventually sink to the bottom by gravitational action. The soil is then contaminated with gross effect upon the terrestrial life. As the evaporation of the volatile lower molecular weight components affect aerial life, so the dissolution of the less volatile components with the resulting emulsified water, affects aquatic life [1]. The harmful effects of oil spill in the environment are many. Oil kills plants and animals in the estuarine zone. Oil settles on beaches and kills organisms that live there. It also settles on ocean floor chains and decreases the yield of edible crustaceans. It also coats birds impairing their flight or reducing the warming property of their feather, thus making the birds more vulnerable to cold. Oil endangers fish hatcheries in coastal waters and as well contaminates the flesh of commercially valuable fish [2]. The removal of oil from waste water is a matter of great interest in the field of water pollution which is a serious cause of environmental degradation. Besides the classical water treatment, bio-sorption of oil on the surface of water is an alternative technique, primarily because it utilizes inactive dead biological materials as sorbents which are generally available at low cost, non-hazardous and abundant in nature [3]. The main draw backs of these plant-derived sorbents are their relatively low oil sorption capacity, low hydrophobicity and poor buoyancy when compared to the synthetic sorbents, such as polypropylene [4]. Once plant-derived sorbents are applied, to saturated environments, preferential water sorption is favored over the sorption of oil, because the sorbents are

hydrophilic in nature. Agricultural bye-products are generally well documented with water sorption and luck of dimensional stability, due to their associated hydroxyl functionalities. These groups are abundantly present in all the three major components of a plant-based material and are responsible for their hydrophilicity [5]. Hydrophobicity (oleophilicity) is one of the major disadvantages of sorbents properties that influence the effectiveness of oil sorption in the presence of water [5]. The effectiveness of the sorbents in saturated environments would be enhanced when the density of the hydroxyl functionality is decreased [6]. The hydroxyl functionality of the plant fibre can be reduced by chemical modification such as acetylation, methylation, cyanoethylation, benzoylation, acrylation and acylation [7]. The acetylation reaction is one of the most common techniques employed for hydrophobic treatment of lignocellulosic materials, which involve a substitution reaction of a hydroxyl group(hydrophilic) into an acetyl group (hydrophobic). This reaction is typically carried out by heating lignocellulosic material in the presence of acetic anhydride, with or without a catalyst. In addition, for the efficient application, data on the sorbent's sorption capacity and a good understanding of the basic mechanism behind the sorption capabilities are required [7].

2. Material and Methods

2.1. Sample Preparation and Treatment

The *Hibiscus sabdariffa* fibre was collected from Gashala Guw, village in Hong local government Area of Adamawa State. Some of the fibre was removed from the stem after the plant has been dried. This was achieved by socking the plant material in water for three to five days (3-5days), it was then removed and the stem separated from the fibre while it was wet. The fibre was washed thoroughly with water to remove dust, fungus, water soluble components and other foreign materials. The washed fibre was dried in sun light for 12h (4h for three days) and then left to dry at 65^0C in an oven. The fibre was reduced in size by the use of piston and motor and then sieved through 20 and 25 British standard sieves (BSS).

2.2. Soxhlet extraction

The plant fibre was extracted using Soxhlet extraction set-up by using small amount of the sample (30g packed in a filter paper) of the sieved material at a time, with a mixture of N-hexane and acetone in the ratio of 1:4, this is, in order to reduce the influence of the fibre extract on acetylation [8]. The extracted fibre sample was then dried in the laboratory oven for about 16h and the extracted content was then calculated, as a percentage of the oven-dried test sample.

2.3. Acetylation process

The acetylation of the plant fibre was done under mild conditions in the presence of NBS using acetic anhydride for acetylation in a solvent free system. The amount of substrate and reactant was combined in the ratio of 1:20 (g dried *Hibiscus sabdariffa* fibre/ml acetic anhydride). The reaction temperature was varied from 30^0C to 80^0C, while the reaction time was between 1-3h and the amount of catalyst was varied from 0 to 3%. The mixture of raw fibre and catalyst was placed in a round bottom flask fitted to a condenser. The flask was placed in an oil bath on top of a thermostatic heating device, the flask was removed thereafter from the water bath and the hot reagent decanted off. The fibre was washed thoroughly with ethanol and acetone to remove unreacted acetic anhydride and acetic acid as by-products. The new product was dried in an oven at 60^0C in oven for 16h prior to analysis. The extent of acetylation was estimated from the infrared spectra by calculating the ratio of the absorption intensities(i) for the vibration signals of C=O, (around 1740-1745cm-1) and C-O (1020-1040cm-1):

Extent of acetylation (EA) = I_{1740}/I_{1020}(1). **Eqn. 1**

2.4. Characterization of the fibre

a. Fourier Transform infrared spectroscopy

The crude and modified form of the fibre was characterized using Fourier Transform Infrared spectrophotometer (FT-IR).

b. Moisture content

The moisture content was determined using the method of Joel *et al*.,[3]. Due to non-availability of the extract, 500mg of the plant fibre was dried at 105^0C for 4h and the percentage moisture was calculated using the following relation:

Moisture (%) = (loss in weight on drying/initial weight of sample) x 100. The procedure was repeated five (5) times and the mean value computed.

c. Ash Content

Ash content was determined using the method employed by Adebajo [9].

d. *Volatile Content.*

500mg of the plant fibre was heated at 300^0C for 10minutes in a partially closed porcelain crucible in muffle furnace, after cooling it and the difference in weight was recorded. The volatile content (Vc) was determined using the method used by Fapetu [10].

e. Fixed Carbon

The fixed carbon content was determine using the formula Fc (%) =100 – Vc – Ac as adopted by Fapetu *et al.,* [10].

f. Bulk Density

The method described by Ekpete and Horsfall [11] was adopted for the determination of the bulk density.

g. Porosity

Porosity was determined by the method adopted by Ekpete and Horsfall [11].

h. Specific Gravity

The method of Bureau of Indian standards (IS 2720, 1980) and Ekpete and Horsfall [11] was adopted.

i. Scanning Electron Microscope (SEM)

Scanning electron microscope (SEM) was used for studying the morphology of the fibre.

2.5. Kinetics of the Acetylation of the Fibre

The kinetics of the acetylation of the *Hibiscus sabdariffa* fibre was studied by fitting the obtained data in rate curves-pseudo first order and intra-particle diffusion.

a. Thermodynamics of *Hibiscus sabdariffa* fibre acetylation

The thermodynamics of the acetylation of the fibre was studied using

$\ln\theta = A-\frac{B}{T}$ **Eqn. 2**

2.6. Statistical Analysis

Analysis of variance (ANOVA) was used to study the effects of time, catalyst and temperature on the degree of acetylation of the Hibiscus sabdariffa L. fibre. The quantitative contributions of catalyst, time and temperature was determined using linear regression.

3. Results and discussion

3.1 Extraction yield and approximate percentage

The result obtained from the extraction of the *Hibiscus sabdariffa L.* gave about 10% of the crude sample as extract obtained from the extraction of the sample. A total of 100 grams of the sample was used for the extraction with the most suitable solvent combination among the solvent used for the extraction and only 10% extracts was obtained. The lower yield of products may be as a result of the nature of the plant that is used for the extraction; that is the fibre which is expected to have low solubility.

3.2 Phytochemical Composition of the Hibiscus sabdariffa fibre

The result obtained from the study of the phytochemical composition of the plant fibre indicated the presence of cellulose, flavonoids as the most common components of the fibre, though it may contain some components which this research has not find out. The fibre content being the highest content of the material is what gives it its strength. The results of the crude/unmodified and acetylated/modified form of the *Hibiscus sabdariffa* fibre. The result indicated that, both the modified and the unmodified form of the fibre has low moisture content, density and specific gravity while on the other hand, it has high fixed carbon content, swelling ability and a moderate volatile content. The plant also indicated an increase in the swelling ability, volatile content and porosity as it moves from unmodified form to the modified form, while it shows a decrease in the ash content, fixed carbon content, moisture content, specific gravity and bulk content. This change is due to the change in the physical properties of the fibre with the acetylation process. This result is similar to that obtained by Donatus [12], on the study of the application of Violet tree root powder as a natural sorbent in oil spill clean-up.

3.3 Acetylation of the Hibiscus sabdariffa L. Fibre

The acetylation of the fibre was done using acetic anhydride in a solvent free system, using acetic anhydride and N-bromosuccinamide as catalyst. The mechanism of the acetylation process was proposed thus: the overall reaction is;

Hibiscus sabdariffa fibre-OH+ H_3C-$COOCOCH_3$ >*Hibiscus sabdariffa* fibre-OCO-CH_3 + HO-$COCH_3$

The mechanism;
Since the reaction is a surface reaction, that is only the surface OH will be affected at the fibre site, thus;

Hs fibre-OH + $H_3CCOOCOCH_3$ {Hsfibre……OH + H_3CCO…….$OCOCH_3$} >

Hsfibre-$OCOCH_3$ +H_3COC-OH.

The reaction is a substitution reaction in which the acetyl group of the acetic anhydride substituted the hydroxyl (OH) group of the fibre to give fibre acetate and a methoxymethanol. The acetyl group that is introduced into the fibre extract being a hydrophobic center is believed to change the property of the fibre from being hydrophilic to hydrophobic. The effects of catalyst, temperature and time on the reaction were studied and it shows that catalyst and temperature have significant effects on the extent of acetylation of the fibre, the variation in the degree of acetylation are not significant. Time on the other hand has no effect the reaction. This may be due to the complex nature of the fibre. Evidence, as reported by Sun and Sun, [8], reveals that, cellulose is the major components of a plant fibre, like *Hibiscus sabdariffa* fibre alongside hemicellulose and lignin. Furthermore, phenolic, benzylic or alcoholic (primary or secondary) hydroxyl groups are present in the lignin region, while only the alcoholic hydroxyl groups are found in the carbohydrate. Phenolic hydroxyl groups are attached to aromatic rings

containing various substituents [13]. The different types of hydroxyl groups will react differently with acetic anhydride. For example, in the study of the acetyl distribution in acetylated (whole) wood and reactivity of isolated wood cell wall components to acetic anhydride [7] observed the order of reactivity to be lignin > hemicellulose > halocellulose (the remaining product after removal of lignin from wood). Cellulose was observed not to react with acetic anhydride in the absence of catalyst. The extent of acetylation was estimated from the infrared spectra by calculating the ratio of the absorption intensities (i) for the vibration signals of C=O, (around 1740-1745cm-1) and C-O (1020-1040cm-1) [7].

Extent of acetylation (EA) = I_{1740}/I_{1020} **Eqn. 3**

3.4 Factors that affects the Acetylation Process

The Acetylation of the *Hibiscus sabdariffa* fibre like any other reaction is being influenced by some factors as observed from the results obtained from this work these factors include temperature, amount of catalyst, acetic anhydride and time. Among these, the effect of temperature, acetic anhydride and catalyst are more prominent on the acetylation process, but time has little or no effect on the reaction.

3.5 Effects of Acetic anhydride on the Acetylation Process

The effect of acetic anhydride on the reaction is constant and directly proportional with respect to the concentration. The reaction being diffusion controlled and a solvent free process, it`s rate depends on the concentration of the acetic anhydride and the sample may dissolving the acetic anhydride at high concentration. Also, since the reaction is a substitution reaction, and the incoming group is from acetic anhydride, the reaction may give a poor yield at a very low concentration of the acetic anhydride. The extent of acetylation may also be affected by the concentration of the acetic anhydride. The combining ratios used for this research work and as adopted by many similar researchers for acetylation of various plants materials is 1:20 (g *Hibiscus sabdariffa* fibre/ml acetic anhydride) and the results was encouraging.

3.6 Effects of Temperature on the Acetylation Process

The effect of temperature on the Acetylation of the *Hibiscus sabdariffa* fibre is presented on figure 1. The result shows some changes in the extent of acetylation of the *Hibiscus sabdariffa* fibre as a result of change in temperature. The research was carried out at different condition of temperature and the result indicated some significance changes in the extent of acetylation, with change in temperature. As the temperature increases, the rate of the acetylation also increases, as a result of increase in the heat content or enthalpy of the reaction which also lead to the increase in the disorderliness of the transition state of the reaction as a result of faster breaking of bonds, and consequently bond formation takes place and the final product is obtained. The increase in temperature, lead to the ease of acetylation due to reaching of the heat of acetylation of the fibre (T_0). The result is similar to that obtained by Nwadiogbu *et al.* [5].

3.7 Effects of Catalyst on the Acetylation Process

The results of the effects of catalyst on the acetylation of the *Hibiscus sabdariffa* fibre is presented on figures 2 and 4 for acetylation processes at 30 and 80^0C respectively at different amount of catalyst while the concentration of the acetic anhydride, amount of the fibre and reaction time are maintained constant. The results showed a significance increase in the extent of acetylation with the increase in the percentage of the catalyst (N-bromo succinamide) used. This is similar with the result obtained by Nwadiogbu *et al* [5] for the acetylation of corn cob, using acetic anhydride in the presence of NBS as catalyst.

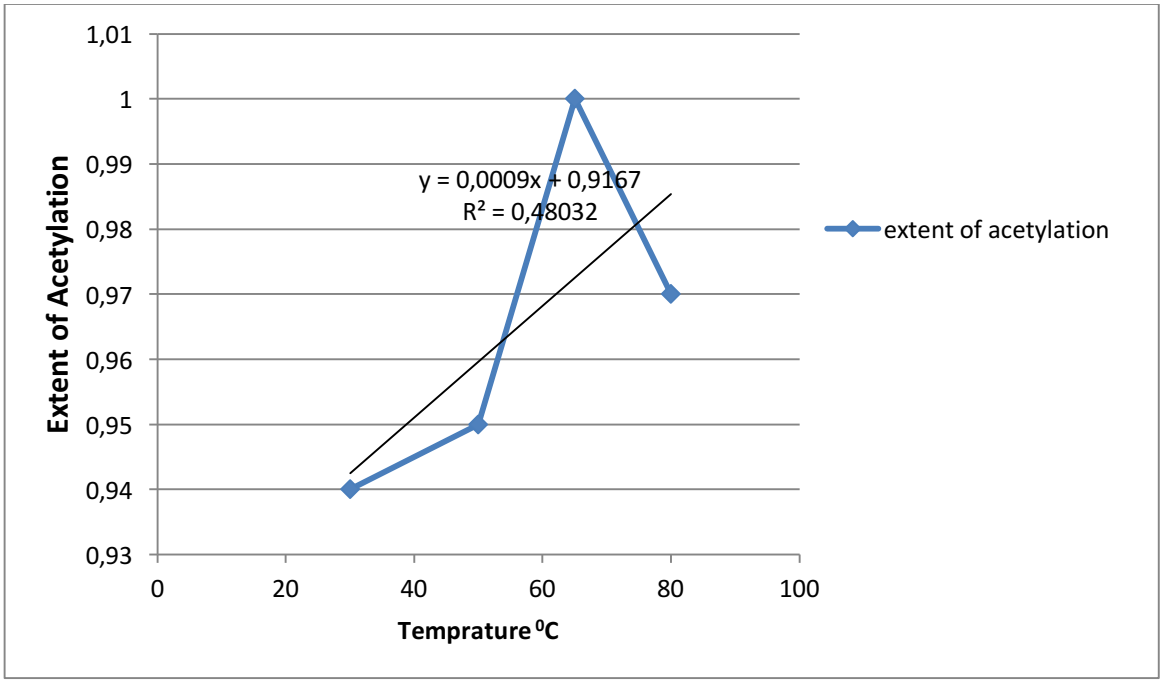

Figure 1. Effects of temperature on the acetylation of *Hibiscus sabdariffa fibre*

Catalyst is a substance that influences the rates of a chemical reaction but remain unchanged at the end of the reaction. Catalyst may/may not participate in a reaction, depending on the situation. In the acetylation of *Hibiscus sabdariffa* fibre, using acetic anhydride, in a solvent free system, N-bromosuccinamide is used as catalyst. The reaction which was carried out at a solvent free system and different amount of catalyst shows a significant increase in the yield of product of the reaction with increase in the catalyst percentage, even at the same condition of temperature.

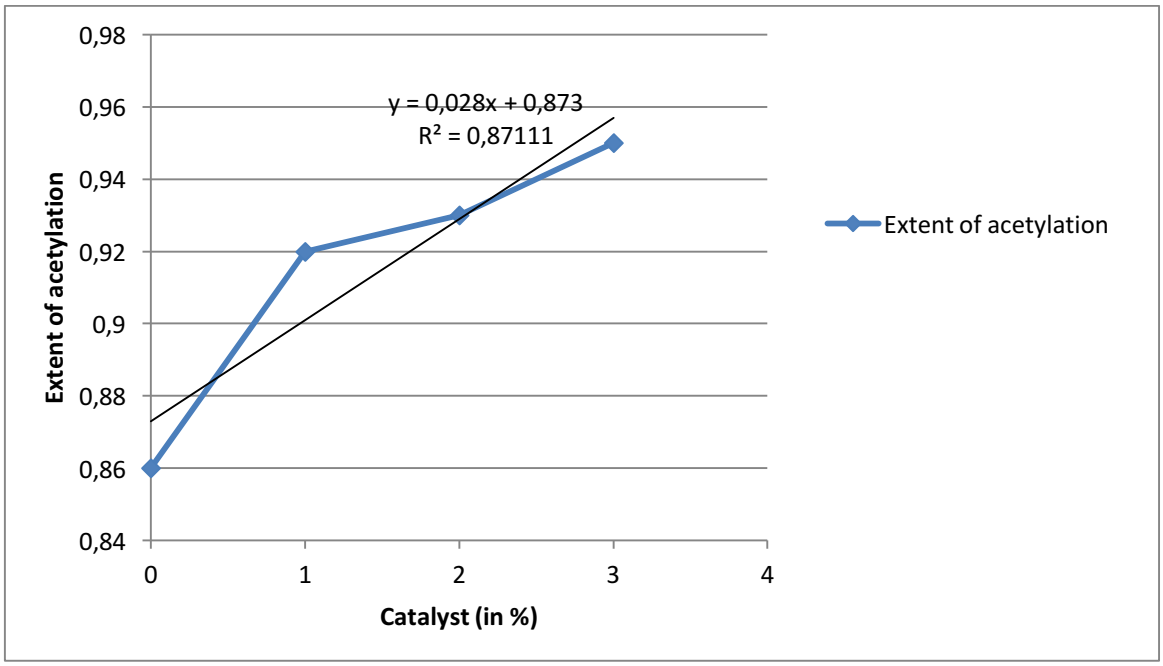

Figure 2. Effect of Catalyst on Acetylation at 30^0C

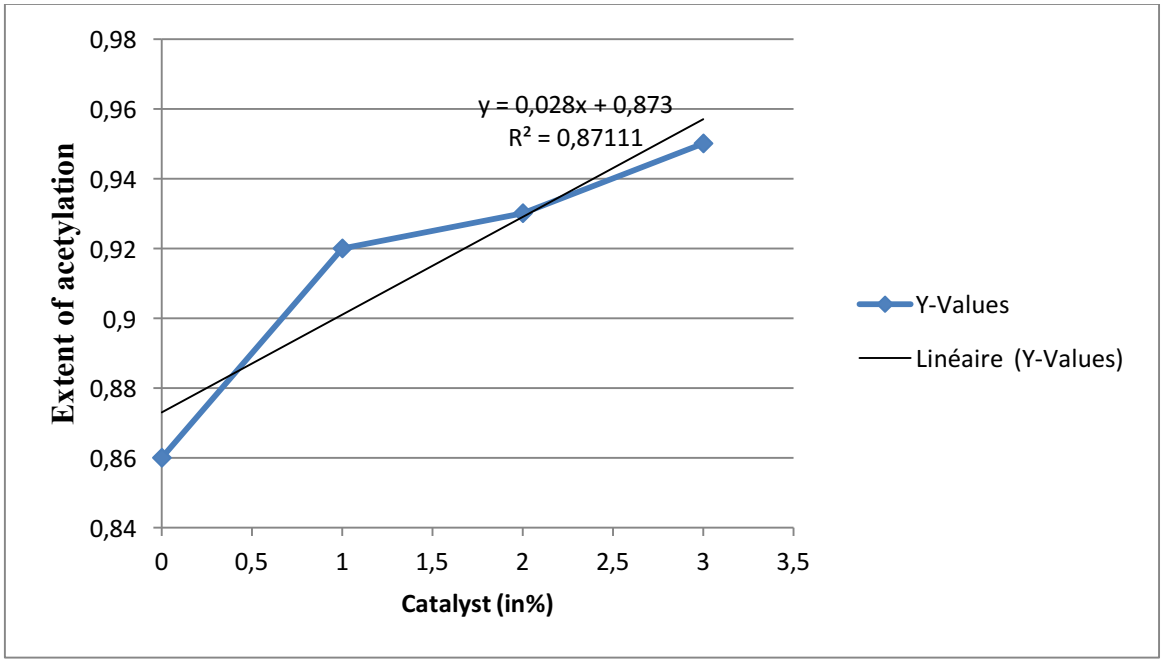

Figure 3. Effects of Catalyst on the Extent of acetylation at 80^0C

3.8 Effects of Time on the Acetylation Process

The result of the effect time on the acetylation process is presented on figure 4. The effect of time on the acetylation of *Hibiscus sabdariffa* fibre, using acetic anhydride in a solvent free system in the presence of N-bromosuccinamide as catalyst, was not significant. The reaction was carried out at different times from 1-3 hours, and the result obtained at different times show no significant changes as the result of change in time, hence, it can be concluded that, the reaction is instantaneous.

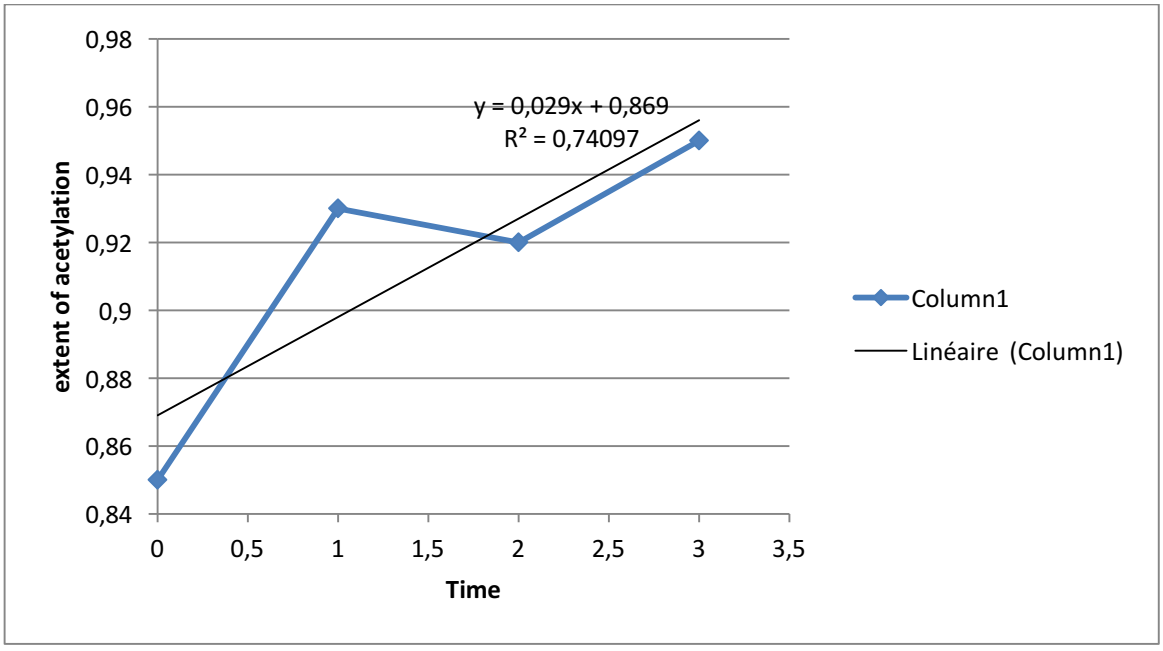

Figure 4. Effect of time on the acetylation of *Hibiscus sabdariffa* fibre

3.9 Fourier Transform Infrared Spectroscopy (FT-IR)

The results of the infrared spectra of both the modified and unmodified form of the *Hibiscus sabdariffa* fibre samples are presented on the IR spectra below. The result shows a significant change of properties

of the sample after the modification, especially with respect to their hydroxyl functionalities and the introduced carbonyl function. These changes will determine the subsequent changes in the behaviour of the fibre in respect to the absorption of oil in aqueous solution. The acetyl group ($CH_3C=O$) being a hydrophobic center, as it replaces the hydroxyl (O-H) group, a hydrophilic center, from the fibre changes its sorption property from the former hydrophilic (oleophobic)to hydrophobic (oleophilic), which is the primary objective of this research. This is an indication that, during the reaction process, some acetyl groups from the acetic anhydride are attached to the fibre at the expense of the hydroxyl groups, a typical substitution reaction. The major changes that occur before and after the treatment are the increase in the IR absorption bands characteristic of the carbonyl (C=O) functional group at (1723-1740cm^{-1}), the C-H absorption peaks at (1373, 1373, 1377, 1375, 1371) and the increase in the intensities of -C-CH_3 and C-O stretching frequencies at (1219, 1239, 1214) which are the indication or confirmation of the formation of ester bands as a result of the acetylation modification process.

On the other hand, the lowering intensities of the characteristic absorption bands of the hydroxyl (O-H) group stretching around (3200-3700cm^{-1}) and O-H out of plane stretching at (1374, 1456, 1375, 1377, 1459cm^{-1}) indicated the reduction of the number of hydroxyl (O-H) groups of the fibre during the modification process. The absence of band at 1700cm^{-1} and 1840-1760cm^{-1} indicated that the modified sample is free of acetic acid as by-product and unreacted acetic anhydride.

The FTIR results of the crude/unmodified fibre indicated a very low carbonyl absorption peak of the carbonyl functional group between 1720-1750cm^{-1}, which is the characteristic absorption band of the ester functional group. The peak height that appears at the region of the ester carbonyl absorption frequency is about 54.2 which is very low. This is an indication of the absence or low carbonyl functional group in the unmodified form of the fibre, which is one the typical characteristics of the plant derived material, which are always short of the carbonyl functions when compared to the hydroxyl functionalities [5]. The FT-IR results of the carbonyl absorption bands of the acetylated/modified form of the fibre indicates a significant increase in the carbonyl absorption peak of the modified form of the fibre when compared to the unmodified fibre. The carbonyl absorption peak of the ester carbonyl functions between 1720-1750cm^{-1} are between 90-101, which is much higher than that of the unmodified form of the fibre which is 54.4. This shows the increasing in the carbonyl absorption frequencies at the carbonyl region. The result also indicated a decrease in the hydroxyl absorption frequencies of the modified form of the fibre.

3.10 The FTIR Region 3700-3200cm^{-1}

This region is characterized by the absorption bands of hydroxyl (O-H) group depending on the hydrogen-bonding, such as the hydrogen bonding of alcohol and phenol, the hydrogen-nitrogen (N-H) of amine and the carbon-hydrogen (C-H) of a methyl stretching bonds.

3.11 The FT-IR Region 3200-2800cm^{-1}

This is a region characterized by the absorption bands of different types of C-H depending on the type of carbon-hydrogen bonds in a given molecule, such as C-H stretching in alkenes (=C-H), C-H stretching in alkanes (-C-H) and C-H stretching in aldehydes (O=C-H).

3.12 The FT-IR Region 2400-2100cm^{-1}

This is a region characterized by the absorption bands of the unsaturated compounds such as amide (–C=N) and carbon-carbon unsaturated (C=C) in alkene.

3.13 The FT-IR Region 1850-1100 cm^{-1}

This is the region characterized by the absorption bands of 5-membered ring ketone, 6-membered ring ketones, aliphatic ketones, α,β-Unsaturated ketones, aryl ketones, esters, carboxylic acids, nitrites, etc.

3.14 Kinetics of the Acetylation of the Fibre

The kinetics of the acetylation of the *Hibiscus sabdariffa* fibre was studied by fitting the obtained data in rate curves-pseudo first order and intra-particle diffusion.

The pseudo-first order equation can be derived thus:

Rate of acetylation ($R_{1)} = d[EA]/dt = - k_1[EA]$ **Eqn. 4**

Where t = time, and $–k_1$ = a constant

On the assumption that the anhydride reagent is present in large quantities for surface –OH groups [14], which is proportional to extent of acetylation. Rearranging eq (1) gives

- $d[EA]/[EA] = k_1dt$ **Eqn. 5**
- solution can be obtained by integrating equation (2)

Eq 1 gives $\int_{[EA]o}^{[EA]1} \frac{d[EA]}{[EA]} = k\ 1\hat{}\int_o^t dt$ **Eqn. 6**

Solution to equation (3)

$-\ln [EA][EA]_t/[EA]_o = k_1t$ **Eqn. 7**

$-\ln [EA]_t = \ln [EA]_o - k1t$ **Eqn. 8**

a. Thermodynamics of the Acetylation of the Fibre

The thermodynamics of the acetylation of the fibre was studied using

$\ln\theta = A-\frac{B}{T}$ **Eqn. 9**

Considering the fact that the anhydride reagent displaces the surface –OH sites and these displacement reactions occur when the *Hibiscussabdariffa* fibre`s pores are covered appropriately and this coverage is dependent on the concentration of the –OH groups [14], which is proportional to the extent of acetylation. Therefore, θ represents surface coverage. There are two unknowns in equation (6) and these makes it difficult to be used directly. However, careful observation enables one to observe that equation (6) is equivalent to Clausius-Clapeyron equation,

$\ln\theta = -\Delta H/RT$ **Eqn. 10**

Where B = ΔH/R and A is the intercept. In fact, equation **Eqn.** 7 is the Gibbs-Helmholtz Equation

$d\ln\theta/dT = -\Delta H/RT^2$ **Eqn. 11**

By integrating equation (8), it gives

$\int_{\theta o}^{\theta T} ln\theta = \Delta H/R \int_{To}^{T} 1/T^2 dT$ **Eqn. 12**

Equation (9) gives

$[dln\theta]_{\theta o} = - \Delta H/R\ [T^{-1}]n\theta]_{\theta o}{}^{\theta T} = - \Delta H/R\ [T^{-1}]^{T}{}_{To}$ **Eqn. 13**a

$\ln (\frac{\theta T}{\theta o}) = - \Delta H/RT + \Delta H/RT_0$ **Eqn. 13**b

$\ln\theta_T = - \Delta H/RT + \Delta H/RT_0 + \ln\theta_0$ **Eqn. 13**c

Eq (10c) allows the plot of $\ln\theta_T$ versus T^{-1} such that -ΔH/R is the slope. B, intercept at/on Y axis (lnθ) gives $\ln\theta_0$, A, and intercept at/on x axis (T^{-1}) gives $\Delta H/RT_0$. ΔH is the heat of the fibre`s acetylation, $T_0$ is the critical temperature of acetylation (below which acetylation of the fibre is not feasible), and $\theta_0$ is the critical degree of the fibre`s acetylation.

It is assumed that the acetylation of the *Hibiscus sabdariffa* fibre should be an equilibrium surface reaction. The value obtained from slope of the graph will help in estimating the heat of acetylation of the fibre. The critical temperature of acetylation and the critical degree of acetylation should be obtained from the intercepts on x and y axis. A positive value of heat of acetylation and very low critical temperature value suggests that, the acetylation process is spontaneous (that is a process which proceed easily) by absorbing heat from the environment. A general trend also exists such that high heat of acetylation of a substance indicates difficulty in acetylating the material; hence, very low heat of acetylation value indicates the ease of acetylating the material. The critical degree of acetylation of the fibre obtained explains the mechanisms of its acetylation, values above it suggests diffusion mechanism and above it suggests surface absorption mechanism.

The heat capacity of *Hibiscus sabdariffa* fibre acetylation at constant pressure can be obtained using

$$\Delta H = \int_{T_1}^{T_2} C_p dT = C_p(T_2 - T_1) \qquad \textbf{Eqn. 14}$$

C_p represent the quantity of heat needed to acetylate the fibre whenever a degree rise in temperature occurs, $(T_2 - T_1)$, represent change in temperature. The in entropy of the acetylation will be obtained using

$$\Delta S = C_p \ln \left(\frac{T_2}{T_1}\right) + R \ln \left(\frac{P_1}{P_2}\right) \qquad \textbf{Eqn. 15}$$

The second term in the right-hand side of equation (12) is expected to vanish as the process will be performed at constant pressure. The value of ΔS obtained at the studying temperature will determine the degree of disorderliness or orderliness of the acetylation process for positive or negative ΔS respectively.

H.s. fibre-OH + H_3C-$COOCOCH_3$ → H.s.-OCOCH3 + $HOCOCH_3$ **Eqn. 16**

Below is an equation which shows or describes the acetylation of the *Hibiscus sabdariffa* fibre (represented as H.s fibre) and shows the acetic anhydride, (the larger molecule) disintegrates into acetic acid (smaller molecule). The disintegration of the acetic anhydride to react with the –OH site of the fibre contributes to increase in the disorderliness of the process.

Another important parameter, the change in Gibb`s free energy (ΔG) can be calculated using

$$\Delta G = \Delta H - T\Delta S \qquad \textbf{Eqn. 17}$$

At the studied temperature, the of ΔG determines whether the reaction is spontaneous or not, for negative and positive of values of ΔG respectively.

$$\Delta S = C_p Ln(T_2/T_1) + R Ln (P_1/P_2) \qquad \textbf{Eqn. 18}$$

But:

$\Delta S = -\Delta H/T$,

By multiplying both sides by –T, we get;

$$-T\Delta S_{total} = -T\Delta S + \Delta H \qquad \textbf{Eqn. 19}$$

Given that temperature is always a positive number,

Therefore, the reaction is spontaneous if

$T\Delta S_{total}$ is negative.

At equilibrium, this term becomes equal to zero (0).

Product of temperature (T) and entropy (S) gives a unit of energy which is proportional to the amount of energy available to do work.

This term $-T\Delta S_{total}$ is usually referred to as Gibb`s energy difference or change in Gibbs free energy (ΔG).

$$\Delta G = \Delta H - T\Delta S \qquad \textbf{Eqn. 20}$$

The ΔG is the energy available for a reaction and it includes the contributions both the enthalpy (H) and the entropy (S) of the system.

For spontaneous reactions, ΔG = negative.

(1) K is positive

(2) At equilibrium, Gibbs free energy = 0 and K = 1.

(3) For reaction favored to move in the reverse direction, ΔG = positive and K is less than one (1).

Note: the value of K can be written in terms of ΔG.

$K = e^{-\Delta G/KT}$ **Eqn. 21**

Hence,

$\Delta G - RTLnK$ **Eqn. 22**

The essential difference between kinetics and thermodynamics as they were utilized in this work are expressed by the fact that chemical kinetics is concerned about the macroscopic process running time whereas the thermodynamics is concerned with the macroscopic properties general regulation and it is only concerned with the initial and final states of the system.

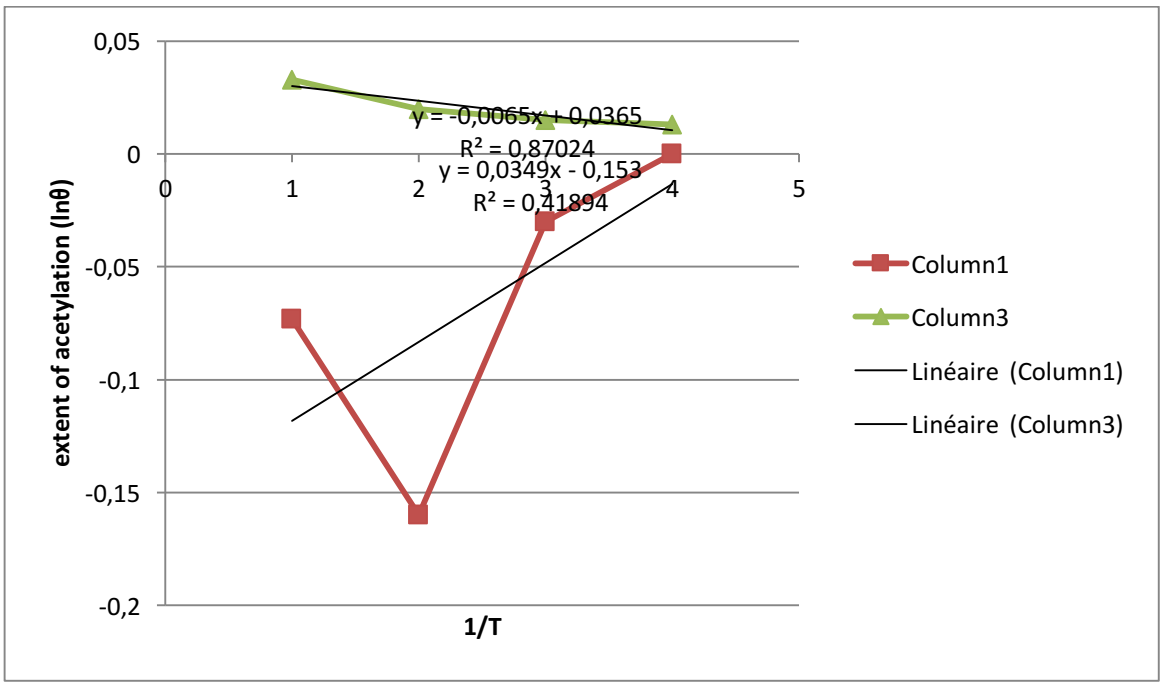

Figure 5. A plot of lnθ against T^{-1}

It is assumed that the acetylation of the *Hibiscus sabdariffa* fibre is an equilibrium surface reaction. The critical temperature of acetylation (T_0) and the critical degree of acetylation (θ_0) are: 0.2328^0C or 273.02328K and 0.94 respectively as calculated from the intercepts on x and y axis respectively. A positive value of heat of acetylation and very low critical temperature value suggests that, the acetylation process is spontaneous (that is a process which proceed easily) by absorbing heat from the environment. A general trend also exists such that high heat of acetylation of a substance indicates difficulty in acetylating the material; hence, very low heat of acetylation value indicates the ease of acetylating the material. The critical degree of acetylation of the fibre obtained explains the mechanisms of its acetylation, values above it suggests diffusion mechanism and above it suggests surface absorption mechanism.

The heat capacity of *Hibiscus sabdariffa* fibre acetylation at constant pressure was obtained using

$\Delta H = \int_{T_1}^{T_2} C_p dT = C_p(T_2 - T_1)$ **Eqn. 23**

C_p represent the quantity of heat needed to acetylate the fibre whenever a degree rise in temperature occurs, $(T_2 - T_1)$, represent change in temperature. The change in entropy of the acetylation was obtained using

$$\Delta S = C_p \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{P_1}{P_2}\right) \quad \textbf{Eqn. 24}$$

The second term in the right-hand side of equation (21) was vanished as the process was performed at constant pressure. The value of ΔS at the studied temperature was 0.0049 which shows that the acetylation process is spontaneous due to the positive value of ΔS.

H.s. fibre-OH + H_3C-$COOCOCH_3$ → H.s.-OCOCH3 + $HOCOCH_3$ **Eqn. 25**

Below is an equation which shows or describes the acetylation of the *Hibiscus sabdariffa* fibre (represented as H.s fibre) and shows the acetic anhydride, (the larger molecule) disintegrates into acetic acid (smaller molecule). The disintegration of the acetic anhydride to react with the –OH site of the fibre contributes to increase in the disorderliness of the process.

Another important parameter, the change in Gibb`s free energy (ΔG) can be calculated using

$$\Delta G = \Delta H - T\Delta S \quad \textbf{Eqn. 26}$$

At the studied temperature, the values of ΔG determines whether the reaction is spontaneous or not, for negative and positive values of ΔG respectively. The values of ΔG at the studied temperature of 30, 50, 65 and 80^0C are: 0.143, 0.045, -0.0285 and -0.102 respectively. This shows that the acetylation of *Hibiscus sabdariffa* fibre is spontaneous due to the negative values of ΔG at 65 and 80^0C and low positive values at 30 and 50^0C respectively.

$\Delta S = C_p Ln(T_2/T_1) + RLn\ (P_1/P_2)$ **Eqn. 27**

But:

$\Delta S = -\Delta H/T$,

By multiplying both sides by –T, we get;

$-T\Delta S_{total} = -T\Delta S + \Delta H$ **Eqn. 28**

Given that temperature is always a positive number,

Therefore, the reaction is spontaneous as

$T\Delta S_{total}$ is negative.

At equilibrium, this term becomes equal to zero (0).

Product of temperature (T) and entropy (S) gives a unit of energy which is proportional to the amount of energy available to do work.

This term $-T\Delta S_{total}$ is usually referred to as Gibb`s energy difference or change in Gibbs free energy (ΔG).

$\Delta G = \Delta H - T\Delta S$ **Eqn. 29**

The ΔG is the energy available for a reaction and it includes the contributions both the enthalpy (H) and the entropy (S) of the system.

For spontaneous reactions, ΔG = negative.

(1) K is positive

(2) At equilibrium, Gibbs free energy = 0 and K = 1.

(3) For reaction favored to move in the reverse direction, ΔG = positive and K is less than one (1).

Note: the value of K can be written in terms of ΔG:

$K = e^{-\Delta G/KT}$ **Eqn. 30**

Hence,

$\Delta G - RT\ln K$ **Eqn. 31**

The essential difference between kinetics and thermodynamics as they are utilized in this work are expressed by the fact that chemical kinetics is concerned about the macroscopic process running time whereas the thermodynamics is concerned with the macroscopic properties general regulation and it is only concerned with the initial and final states of the system.

3.15 Statistical studies of the acetylation process

3.15.1 Analysis of variance

The observed effects of temperature, catalyst and time on the acetylation of *Hibiscus sabdariffa* fibre were tested for significance difference and the ANOVA. The effects obtained from the statistical analysis of the three possible factors: temperature, catalyst and temperature are 0.01, 0.04 and -0.03 respectively. This shows that, the effects of catalyst and temperature are significant on the acetylation of the *Hibiscus sabdariffa* fibre, while the effect of time is not significant.

The value at 5% significance level is 3.37, which shows that the result is significant as the value of F calculated (1.69) is less than the F.

3.16 Scanning electron microscope (SEM) results

The results of the scanning electron microscope (SEM) are presented in the appendix in pictures and fibre histogram. The fibre images as indicated by the pictures shows the pore sizes on the modified and unmodified form of the fibre which are indications of the morphology or physical forms of the fibre that interacts with the electron beams of the scanning electron microscope and produce the signal that produce the images corresponding to the physical components of the fibre.

The morphology of the modified fibre at 65^0C, which appear to have larger pore sizes and more disordered while the unmodified fibre appears to be smooth with smaller pore sizes. The fibre zip also shows the morphology of the fibre indicating the pore sizes with the respective figures. The fibre histogram also gives more explanation about the properties of the modified and unmodified form of the fibre.

Conclusion

In conclusion, the modification of the *Hibiscus sabdariffa* fibre by acetylation was successful as indicated by its IR absorption bands and its sorption behaviour in both oil and water. This is due to the increase in the hydrophobic property of the fibre. Thus, the hydrophobic treatment of a plant such as *Hibiscus sabdariffa* fibre is a suitable method for producing an environmentally friendly, low cost, less hazardous and biodegradable sorbents for oil spill clean-up in aqueous environment, due to its hydrophobic and oleophilic properties.

These plants derived sorbents can replace the synthetic sorbents due to its biodegradability, availability, less hazardous nature unlike the synthetic sorbents materials which are expensive and non-biodegradable.

Conflict of Interest

No conflict of interest declared.

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