Journal of Environmental Chemical Engineering 4 (2016) 3205–3216

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

An approach for the reuse of *Dacryodes edulis* leaf: Characterization, acetylation and crude oil sorption studies

Nnaemeka J.N. Nnaji[a,*], Thereasa U. Onuegbu[b], Obiageli Edokwe[b], Godwin C. Ezeh[c], Adaeze P. Ngwu[d]

[a] Department of Chemistry/Biochemistry/Molecular Biology, Federal University Ndufu Alike Ikwo, Ebonyi, Nigeria
[b] Department of Pure and Industrial Chemistry, Nnamdi Azikiwe University, Anambra, Nigeria
[c] Center for Energy Research Development, Obafemi Awolowo University, Osun, Nigeria
[d] Department of Industrial Chemistry, Caritas University, Enugu, Nigeria

ARTICLE INFO

Article history:
Received 1 March 2016
Received in revised form 5 June 2016
Accepted 8 June 2016
Available online 2 July 2016

Keywords:
Dacryodes edulis leaf
Acetylation
Crude oil sorption

ABSTRACT

This work investigated the modification of Dacyodes edulis leaf (DEL) by acetylation to give acetylated Dacryodes edulis leaf (ADEL) and their applications to treatment of crude oil polluted waters. DEL acetylation was favoured by low temperature, increased time of acetylation, and in the absence of catalyst. Crude oil sorption kinetic data were best fitted by liquid film diffusion and pseudo-first order kinetic models for DEL, but pseudo-second order kinetic model best fits crude oil sorption data by ADEL. Equilibrium crude oil sorption data were best fitted into Langmuir and Freundlich isotherms for ADEL and DEL respectively. Results suggest that ADEL is more suitable for crude oil sorption than DEL, therefore, possesses more potential for application in treatment of oil spillage.

1. Introduction

Crude oil exploration is an important activity of man considering that it is a major source of energy for vehicular, domestic and industrial activities. Consequently, crude oil explorations often cause spills that result in pollutions of affected sea and land regions. Aquatic lives, vegetation and man have suffered severely from crude oil pollutions there is therefore the need to direct recent research towards discovering efficient materials for clean-up of crude oil polluted waters (COPOWs). However, materials which are biodegradable, cheap, environmentaly friendly and readily available make this area of scholasticism challenging. Interestingly, the use of agricultural by-products meet these required attributes, therefore, they are reportedly in vogue for applications in clean-up of COPOWs [1–3]. Chemical modification, by acetylation, of agricultural byproducts have been reported to enhance the effectiveness of the materials by decreasing the density of the hydroxyl functionality [4]. Examples of acetylated materials used for crude oil sorption studies include: corncobs, rice husks, banana fibre [2,3,5] and kapok fiber for gasoline oil [6]

Plants are important in our everyday existence. They provide our foods, produce the oxygen we breathe, and serve as raw materials for many industrial products such as clothes, foot wears and so many others. Plants also provide raw materials for our buildings and in the manufacture of biofuels, dyes, perfumes, pesticides, adsorbents and drugs. *Dacryodes edulis*, however, is an odiferous fruit tree found in equatorial and humid tropic climates and originates from Central Africa and Gulf of Guinea area [7]. Much work has been done on *Dacryodes edulis*. For example, Ikhuoria and Maliki [8] characterized the oil from *Dacryodes edulis* pear, Okwu and Nnamdi [9] investigated the phytochemical contents and medicinal values of *Dacryodes edulis* exudates. The inhibitive effect of exudate gum from *Dacroydes edulis* on the acid corrosion of aluminium was studied by Umoren and co-workers [10]. Also, Oguzie et al. [11] studied DEL extract as an alternative steel corrosion inhibitor. However, there appears not to be any work(s) on the application(s) of *Dacryodes edulis* leaf (DEL) in crude oil polluted water.

Classes of oil sorbents may include organic synthetic [12], inorganic mineral and agro-based products [13]. Notably, many organic synthetic products such as polypropylene and polyurethane, used as commercial oil sorbents present challenges because they are relatively expensive [14] and pose disposal problems due their xenobiotic nature [15]. Teas et al. [16] reported perlite, graphite, clay and so on as examples of inorganic mineral oil

* Corresponding author.
E-mail address: joemeks4u@yahoo.com (N.J.N. Nnaji).

http://dx.doi.org/10.1016/j.jece.2016.06.010
2213-3437/

sorbents which possess environmental disposal challenges caused by slow degradation [16]. Agro-based products are the class of sorbents which now attract great interest because of their improved properties over the organic synthetic and inorganic mineral sorbents. Amongst these properties are: good oil absorbency, ready availability, inexpensive and cost savings in disposal fee [15]. Consequently, studies on some agro-based oil sorbents such as kapok, milkweed and cotton, were carried out and results suggest that they possess good oil sorption properties [15,17].

On one part, the purpose of this work is to assess the physico-chemical properties of Dacryodes edulis leaf (DEL) for its use as an environmental clean-up raw material for crude oil polluted water. On another part, the modification of DEL by acetylation, the mechanism and thermodynamics of the process were monitored in detail. Also, detailed kinetic and equilibrium studies of crude oil and water sorptions by DEL and ADEL were done.

2. Materials and methods

2.1. Material preparation

DEL was sourced locally from beneath trees near the University of Nigeria Nsukka campus. Thorough washing was done with water and properly air dried (during harmattan). They were size reduced and sieved through 20 and 25 British Standard Sieve (BSS Sieves) so that particle sizes in the range $707 - 841\mu\mu$ were used. Reagents and chemicals, of analytical grades, used were from British Drug House (BDH) and include acetic anhydride, N-Bromosuccinimide (NBS), Acetone, Ethanol and *n*-Hexane, and were used without further purification.

The sieved material (100 g) was extracted with a mixture of acetone and *n*-hexane ($4:1\frac{v}{v}$) for 5 h (to reduce the influence of the fibre extractibles on acetylation), dried in a laboratory oven (operated in the range of 60–70 °C) for 16 h and stored in a desiccator at room temperature thereafter. The extractible content was calculated on a percentage of the oven-dried test samples.

2.2. Methods

2.2.1. Characterisation of DEL

2.2.1.1. Density determinations. 20 g of the sample was used to fill up a container of 100 mL volume and the bulk density was then calculated using the following expression [18]:

$$\text{Bulk density} = \frac{w}{v} \tag{1}$$

where w is weight of the sample and v is volume of the container.

After two hundred 'taps, mechanically, a new volume (v_{200}) was obtained. The mechanical tapping was performed by raising the cylinder and allowing it to drop through a safe height, under its own mass. Tapped density was calculated using the following expression

$$\text{Tapped density} = \frac{w}{v_{200}} \tag{2}$$

where w is weight of the sample and v_{200} is 'tapped' volume of the container.

As described by Ejikeme [18], true density was determined by the liquid displacement method using xylene as the immersion fluid. True density was calculated using the following expression

$$\text{Time density} = \frac{w}{v_T} \tag{3}$$

where w is weight of the sample and v_T is 'true volume of the container.

2.2.1.2. Determination of percentage ash content. 2.0 g of the sample was weighed into a pre-weighed crucible and burnt over a Bunsen burner flame until there was no more smoke. The sample was then placed in the muffle furnace at 600 °C until it turned grey-white. This was cooled in a dessicator and weighed to a constant weight. The following expression was used to calculate ash content [19]:

$$\text{Ash content}(\%) = \frac{w_{ash}}{w_{sample}} \times 100 \tag{4}$$

where w_{ash} is weight of ash and w_{sample} is weight of sample.

2.2.1.3. Percentage moisture content. 2 g of the ground sample was weighed into a pre-weighed crucible. The crucible and the content were weighed again. This was then put in the oven at 101 °C for 2 h after which it was removed, cooled and weighed until a constant weight was obtained. The expression used to calculate the moisture content is [19]:

$$\text{Moisture content}(\%) = \frac{w_{sample} - w_{dry}}{w_{sample}} \times 100 \tag{5}$$

where w_{sample} is the weight of sample before drying, w_{dry} is weight of sample after drying.

2.2.1.4. Determinations of cellulose, hemicellulose and lignin. Compositions of cellulose, hemicellulose and lignin in DEL were determined as described elsewhere [5].

2.2.2. Determination of mineral composition

Available XRF equipment is portable AMPTEK(R) for Energy Dispersive X-ray Fluorescence (EDXRF) measurements. Sample preparation was done by pulverizing the sample to fine powdery form using an agate mortar and a pellet of the sample was formed using a CARVER model manual pelletizing machine at a pressure of 6-8 Torr. The pelletized sample was inserted into the sample holder of the XRF system and was bombarded by X-ray fluorescence spectrometer with a Ag anode at a voltage of 25 kV and current of 50 μA for 1000 counts or approximately 18 min in an external chamber setup. The equipment model is PX 2CR Power Supply and Amplifier for XR-100CR Si-pin Detector. Characteristic X-ray of the sample was detected by the solid state Si-Li detector system and spectrum acquisition was done using ADMCA[R]software. The spectrum analysis was done using the ADMCA plus Fundamental Parameter (FP-CROSS) software which translates the peak areas into concentration values.

2.2.3. Acetylation of DEL

The method of Nwadiogbu et al. [2] was adopted for DEL acetylation as briefly described. The combination ratio during acetylation was in a ratio of 1:20 ($^{w}/_{v}$ of DEL: acetic anhydride). Respectively, the reaction temperature, time and amount of catalyst (NBS) were varied from 30 °C to 100 °C, 1 h to 3 h and 0–4%. After acetylation, DEL was thoroughly washed with ethanol and acetone to remove unreacted acetic anhydride and acetic acid (as by-product). The new product, acetylated dacryodes edulis leaf (ADEL), was dried in an oven at 60 °C for 16 h prior to analysis. The extent of acetylation was determined from the infrared spectra of ADEL samples by calculating the ratio of the intensity of the acetyl C=O band (around 1740–1745 cm^{-1}) to the intensity of the C—O signals of cellulose (at about 1020–1040 cm^{-1}) [20]:

$$R = \frac{I_{1740}}{I_{1020}} \tag{6}$$