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Thermodynamic parameters for the adsorption of volatile n-alkane hydrocarbons on water hyacinth (*Eichhornia crassipes*) root biomass: Effect of organic solvent and mineral acid treatment

Netai Mukaratirwa-Muchanyereyi[1,2], Jameson Kugara[1] and Mark Fungayi Zaranyika[1]*

[1]Chemistry Department, University of Zimbabwe, P. O. Box MP 167, Mount Pleasant, Harare, Zimbabwe.
[2]Bindura University of Science Education, Bindura, Zimbabwe.

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The use of lignocellulosic fibres as biosorbents has both environmental and economic benefits. They are biodegradable, safe to use and most importantly renewable and less costly than synthetic fibres. The objectives of the present work were to study the performance of lignocellulosic fibres from water hyacinth (*Eichhornia crassipes*), a pervasive fresh water aquatic weed widely distributed in the tropics, as a biosorbent for n-alkane hydrocarbons, n-hexane to n-nonane. The free energy (ΔG_a), enthalpy (ΔH_a) and entropy (ΔS_a) for the adsorption of n-alkanes hexane to nonane on ground dried water hyacinth (*E. crassipes*) root biomass were studied between 40 and 70°C column temperature using inverse gas chromatography, before and after treatment of the root biomass with mineral acid and organic solvent. The free energy of adsorption (ΔG_a), enthalpy of adsorption (ΔH_a) and entropy of adsorption (ΔS_a) values of -20.42 to -35.992 kJ.mol^{-1}, -21.18 to -33.704 kJK^{-1}mol^{-1} and +0.0023 to +0.0041 kJ.mol^{-1} respectively, were obtained for the adsorption of the n-alkane series on untreated water hyacinth root biomass. Mineral acid and organic solvent treatment leads to greater adsorption bond strength, with ΔG_a and ΔH_a values of -36.08 to -38.52 kJ.mol^{-1} and -34.01 to -36.33 kJK^{-1}mol^{-1}, respectively, after mineral acid treatment, and -40.98 to -46.7 kJ.mol^{-1} and -38.35 to -43.7 kJK^{-1}mol^{-1}, respectively, after organic solvent treatment. The results show that mineral acid and organic solvent treated water hyacinth root biomass has potential as biosorbent for the adsorption of volatile n-alkane hydrocarbons. Factors affecting the adsorbent-adsorbate interaction are discussed.

Key words: Water hyacinth, inverse gas chromatography, adsorption free energy, adsorption enthalpy, hydrocarbons.

INTRODUCTION

The use of lignocellulosic fibres as biosorbents has both environmental and economic benefits. They are biodegradable, safe to use and most importantly renewable and therefore much less costly than synthetic fibres.

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*Corresponding author. E-mail: zaranyika@science.uz.ac.zw. Tel: +263 772 252713.

It is for these reasons that lignocellulosic fibres are being targeted for use in various fields (Cordeiro et al., 2011a). Lignocellulosic fibres that have been in commercial use for a long time include flax (*Linum usitatissimim*), hemp (*Cannabis sativa*), kenaf (*Hibiscus cannabinus*), agave (*Agave Americana*), pine apple (*Ananas cmosus*) and sisal (*Agave sisalana*) (Cordeiro et al., 2011a). Non-conventional, low-cost lignocellulosic fibres that have been studied include agricultural wastes, fallen tree leaves, water hyacinth, algal biomass, among others (Rafatullah et al., 2010).

The performance of lignocellulosic adsorbents depends on the nature of the adsorbent and adsorbate. Lignocellulosic fibres can be considered as naturally occurring composites, consisting mainly of helically wound cellulose microfibrils bound together by lignin and hemicellulose. Hemicellulose molecules are hydrogen bonded to cellulose, and act as cementing matrix between cellulose microfibrils. It is highly hydrophilic, partly soluble in water, soluble in alkalis and easily hydrolysed in acids (John and Thomas, 2008; Spinace et al., 2009).

Lignin is a complex three-dimensional hydrocarbon copolymer of aliphatic and aromatic constituents of very high molecular weight. Lignin is completely amorphous, hydrophobic in nature, and is not hydrolysed by acids. It is not soluble in most acids, but soluble in alkalis (Spinace et al., 2009). The chemical composition of lignocellulosic fibres also depends on the conditions under which the plant grew, as well as the origin of the fibre, that is, whether leaf, bast, fruit or root. Crystallinity and surface composition also affect the adsorbents properties of lignocellulosic fibres. These properties can be affected by any chemical treatment or modification that the fibres are subjected to.

Lignocellulosic fibres contain strongly polarized hydroxyl groups, hence natural untreated lignocellulosic fibres are hydrophilic (Cordeiro et al., 2011a). Alkaline treatment leads to the removal of lignin and hemicelluloses which are amorphous, resulting in the increase in crystallinity of the fibres.

On the other hand, dilute acid treatment removes hemicelluloses components of the fibres, leading to the exposure of cellulose (Irfan et al., 2011). Subjecting lignocellulosic fibres to extraction with organic solvents has been reported to lead to an increase in the dispersive component of surface energy as a result of the removal of low molecular components at the fibre surface, such as fatty acids, and exposure of cellulose chains (Belgacem et al., 1995, 1996; Gamelas, 2013).

The properties of adsorbents are often studied using inverse gas chromatography (IGC) (Gamelas, 2013; Dorris and Gray, 1980; Schultz et al., 1987; Askin and Yazici, 2005; Reidel and Mutuana, 2006; Cordeiro et al., 2011a, b; Steele et al., 2008; Bilgic and Askin, 2003; Tshabalala and Wang, 2004; Widegren and Bruno, 2011; Kunaver et al., 2004; Kandor and Dallos, 2014). IGC is in fact gas-solid chromatography in which the interactions between the adsorbent used as solid stationary phase, and the adsorbate used as eluent, are the subject of investigation. This is done by injecting volatile molecules of the eluent and noting the retention times. The thermodynamic properties of the interaction between the solid stationary phase and the eluent are then inferred from the retention volume. The thermodynamic parameters measured are the adsorption free energy, adsorption enthalpy, adsorption entropy and the dispersive component of surface energy of the adsorbent (Reidl and Matuana, 2006). The enthalpy of adsorption is a thermodynamic measure of the strength of the adsorption interaction. IGC experiments are usually performed using a series of n-alkanes (hexane to decane) as non-polar probes; and a series of polar probes consisting of acidic probes (dichloromethane and trichloromethane), basic probes (diethyl ether and tetrahydrofuran) and amphoteric probes (acetone and ethyl acetate) (Shi and Qi, 2012). The choice of IGC probe thus represents the properties of the adsorbate as regards polarity and acid-base properties.

In this paper we report the results of the work we carried out to evaluate the thermodynamic parameters for the adsorption of volatile n-alkane by water hyacinth root biomass. Water hyacinth *(Eichhornia crassipes)* is a floating aquatic weed belonging to the pickerelweed family, *Pontederiaceae,* found throughout the tropics. It is listed as one of the most productive plants on earth, and is considered the worst aquatic weed, that can tolerate a considerable variation in nutrients, temperature and pH (Rajamohan, 2009). Water hyacinth is cheap and easily available, and therefore qualifies as a non-conventional low-cost adsorbent (Tahir and Alam, 2014). It has flourishing roots composed mainly of cellulose and lignin (Zheng et al., 2009).

The adsorbent properties of water hyacinth biomass towards heavy metals have been studied by several researchers (Zheng et al., 2009; Hasan et al., 2010; Ibrahim et al., 2012; Mahamadi and Nharingo, 2007, 2010a, b), and was reviewed by Mahamadi (2011). The review covered sorption dynamics, effect of physical and chemical treatment, pH, temperature, initial metal concentration and biosorbent dose, and concluded that the plant showed excellent biosorbent properties towards several metals of environmental concern, and that pH, temperature, adsorbent dose significantly affected its capacities as metal biosorbent. The review also concluded that further investigations were required on the structural properties of the biosorbent and biosorbent modification. The biosorption of organic compounds by water hyacinth biomaterial has also been studied. Tarawou et al. (2007) and Rajamohan (2009) studied the adsorption of methyl red and congo red dyes by water hyacinth roots as a function of pH, contact time and dye concentration, and showed that equilibrium was reached in about 3 h and fitted the Redlich-Peterson and Freundlich isotherms. The optimum pH was found to be

6.0. Khan et al. (2012) and El-Khalary (2007) studied the adsorption of methylene blue onto water hyacinth biomaterial.

Adsorption equilibrium data fitted the Langmuir isotherm, consistent with monolayer adsorption mechanism. Water hyacinth has also been studied for the removal of phenols from polluted water by Wolverton and McKown (1976), who concluded that 2.75 g of water hyacinth biomass could absorb 100 mg of phenol per 72 h from distilled water and river water.

The aim of the present study was to evaluate the thermodynamic parameters (free energy, enthalpy and entropy) for the adsorption of n-alkane hydrocarbons on untreated, acid treated and solvent extracted water hyacinth root biomass. Hydrocarbons are important water and air pollutants in the petroleum production and distribution industries.

Drinking water sources are often polluted by hydrocarbons in run-off from petroleum fuel distribution centres (storage depots and service stations) and precipitation of emissions from vehicles and air planes, as well as emissions from boats. The thermodynamic parameters for the adsorption of hydrocarbons by water hyacinth root biomass have not been studied previously.

Theoretical

Adsorption partition coefficient, K_R

In gas solid chromatography, the distribution of a solute between the solid stationary phase, S, and the mobile phase, M, at constant temperature and pressure, corresponds to an equilibrium when the solute free energy is at a minimum (Laub and Pecsock, 1978). Under these conditions, its chemical potential, μ in the mobile phase is equal to that in the stationary phase, that is,

$$\mu_S = \mu_M \tag{1}$$

The chemical potential is related to solute activity, *a*, by Equation 2:

$$\mu_i = \mu_i^o + RT \ln a_i \tag{2}$$

Therefore assuming $a_i \approx C_i$, where, *C* = concentration, Equation 1 becomes,

$$\mu_S^o + RT \ln C_S = \mu_M^o + RT \ln C_M \tag{3}$$

Therefore,

$$\frac{\mu_S^o - \mu_M^o}{RT} = \ln C_M - \ln C_S = \ln\left(\frac{C_M}{C_S}\right)$$

And

$$\frac{C_M}{C_S} = \exp\left(\frac{\Delta\mu^o}{RT}\right) = K_R \tag{4}$$

Where, $\Delta\mu^o = \mu_S^o - \mu_M^o$

Adsorption thermodynamic parameters

From thermodynamics, the adsorption free energy, ΔG_a, is given by:

$$\Delta G_a = -RT \ln K_R \tag{5}$$

It can be shown that in gas solid chromatography (GSC), K_R is also given by (Laub and Pecsock, 1978):

$$K_R = \frac{V_N}{A_S} \tag{6}$$

Where, V_N = net retention volume of mobile phase, and A_S = surface area per gram of adsorbent. Hence Equation 5 can be expressed as:

$$\Delta G_a = -RT \ln\left(\frac{V_N}{A_S}\right) = -RT\left(\ln V_N - \ln A_S\right) \tag{7}$$

Therefore

$$\ln V_N = -\frac{\Delta G_a}{RT} + C \tag{8}$$

where $C = \ln A_S$ = a constant. Hence a plot of ln V_N versus $1/T$ should yield a linear plot of slope = $-\Delta G_a/R$. The adsorption enthalpy and entropy are obtained from Equation 9:

$$\Delta G = \Delta H - T\Delta S \tag{9}$$

MATERIALS AND METHODS

Equipment

A Varian 3400CX gas chromatograph equipped with a flame ionization detector (Varian Chromatographic systems, Walnut Creek, California, USA) was used. The IGC experiments were carried out using stainless steel columns 90 cm x 2.1 mm ID (Sigma-Aldrich, Germany) packed with 150 - 212 μm ground untreated, acid and solvent treated dried water hyacinth root biomass. High purity nitrogen from a nitrogen gas generator (M4NT-

Table 1. BET analysis results.

Parameter	Natural	Nitric acid treated	Solvent extracted
Surface area (m^2/g)	3.8189	4.1978	5.0007
Pore volume (cm^3/g)	0.022364	0.024752	0.022228
Pore size (nm)	22.85328	22.94710	17.68746

Table 2. Mean retention times (mins) (n = 3) for volatile n-alkanes on untreated water hyacinth root biomass as IGC stationary phase.

Temperature	n-hexane	n-heptane	n-octane	n-nonane	n-decane
40	0.70±0.00	1.03±0.10	1.87±0.07	4.40±0.32	8.94±0.46
50	0.66±0.04	0.84±0.01	1.41±0.06	2.92±0.03	5.80±0.34
60	0.55±0.02	0.67±0.03	0.95±0.03	1.75±0.13	4.01±0.20
70	0.54±0.00	0.61±0.02	0.87±0.02	1.31±0.01	2.49±0.17

1, Toyo Electric Ltd, Japan) was used as carrier gas. Sieves, 150 and 212 µm (BS410/1986, Endecotts Ltd, London, England) were used to sieve the water hyacinth root biomass after grinding. A Hamilton GC syringe, 1.0 µL, (Sigma Aldrich, Germany) was used for the IGC injections. Brunauer-Emmett-Teller (BET) surface parameters measurements were carried out using a TriStar Model 3000 instrument (Micrometrics Instrument Corporation, Georgia, USA).

Water hyacinth root biomass

Water hyacinth plants were collected from Waerera River, Bindura, Zimbabwe, at Universal Transverse Mercator (UTM) coordinates of (318500;8078400). At the laboratory, the plants were washed with tap water several times, and then washed with distilled water. The roots were separated from the tops, cut into pieces and air dried for several days. The root samples were then ground using a mortar and pestle (Rajamohan, 2009), and then sieved first through the 212 µm sieve, and then the 150 µm sieve, retaining the 150 to 212 µm fraction.

IGC probes

N-hexane, n-heptane, n-octane, n-nonane and n-decane (Analytical grade, Sigma-Aldrich, Germany) were used as non-polar probes (Cordeiro et al., 2011a). Methane (99.99%, Fedgas, Johannesburg, South Africa) was used as the non-interacting probe (Cordeiro et al., 2011a).

Procedures

Solvent extraction

Samples of dried water hyacinth root biomass, 150 to 212 µm particle size, were successively extracted for 24 h in a Soxhlet apparatus, with toluene/ethanol (2:1,v/v) followed by ethanol. Each sample was filtered under suction, rinsed with boiling water, and then transferred to an Erlenmeyer flask containing boiling water. The flask was placed in a hot water bath and left to boil for approximately 1 h. The extracted sample was filtered under suction and air dried for 48 h. The dry sample was stored in a sealed glass jar.

Acid treatment

The water hyacinth root biomass powder was acid-washed by soaking in 0.1 M HNO_3 for 24 h, followed by washing with deionised water, and drying at 65°C for 24 h (El-Khalary, 2007).

Brunauer-Emmett-Teller (BET) surface area analysis

The surface area, pore volume and pore size of the water hyacinth biomass before and after treatment was measured by N_2 adsorption/desorption measurements using the TriStar instrument model 3000 at 373K. Before measurements, all samples were dried at 90°C for 48 h, then 0.1740 to 0.1857g of the sample was put in the tubes of the instrument and degassed for 24 h using a vacuum. The results obtained are shown in Table 1.

Inverse gas chromatography

IGC chromatograms were obtained under the following GC conditions: carrier gas flow rate: 6.4 ml/min; detector and injector temperature: 220°C; column temperature: isothermal at 40, 50, 60 and 70°C. The column was conditioned for 2 h prior to injecting the probes. 0.2 µl of the probe was injected each time. At least three injections were made for each probe at each column temperature. Figure 1 shows typical chromatograms obtained for n-heptane on untreated, acid treated and organic solvent treated water hyacinth root biomass. Table 2 shows typical mean retention times obtained on untreated water hyacinth root biomass. Figure 2 shows typical regression curves obtained when lnV_n values for n-hexane and n-heptane are plotted as a function of $1/T$ for the untreated water hyacinth root biomass. The ΔG_a values calculated for the untreated, acid and solvent treated water hyacinth root biomass from the slopes of the plots of lnV_n as a function of $1/T$ according to Equation 8 are shown in Table 3.

Equation 9 shows that the values of ΔH_a and ΔS_a for the adsorption of the n-alkanes can be obtained from the slope and intercept respectively of the plot of $\Delta G_a/T$ as a function of 1/T. Linear plots (R^2 = 0.9983 to 0.9995) were obtained in all cases.

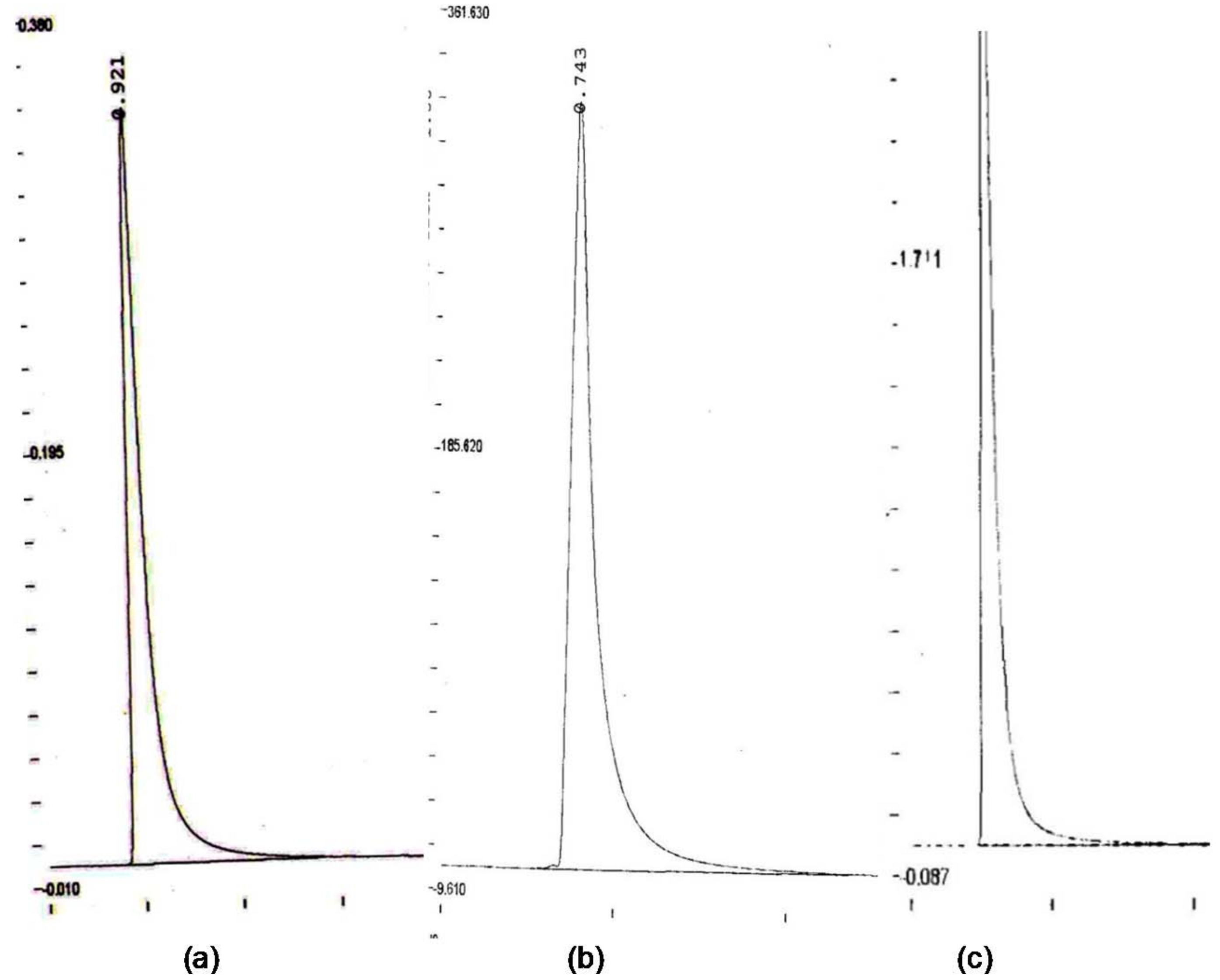

Figure 1. Chromatogram of n-heptane at a flow rate of 6.4 ml/min: (a) Untreated at 40°C, (b) solvent treated at 70°C and (c) nitric acid treated at 70°C.

The ΔH_a and ΔS_a values obtained are shown in Table 3.

RESULTS AND DISCUSSION

Adsorption thermodynamic properties

Untreated water hyacinth root biomass

From Figure 1, it is apparent that sharp peaks were obtained for n-alkane hydrocarbons, although they show some tailing, due to surface adsorption. The retention data obtained (Table 2), shows good reproducibility, with relative standard deviation in the range 0.0 to 10%. The plot of lnV_n versus $1/T$ for all the alkane probes used in the IGC experiments showed good linearity (R^2 = 0.9032 - 0.999), as predicted by Equation 8 (Figure 2). Adsorption free energy values, ΔG_a, obtained for the non-polar probes range from -20.42 kJ.mol^{-1} for hexane to -44.44 kJ.mol^{-1} for nonane (Table 3). When $\Delta G_a/T$ was plotted as a function of $1/T$ for the n-alkanes hexane to nonane, linear plots were obtained (R^2 = 0.9983 -0.9995) (Figure 3), from which the value of ΔH_a are obtained as -21.18, -30.74, -33.62 and -45.84 kJK^{-1}mol^{-1}, respectively for n-hexane, n-heptane, n-octane and n-nonane. The corresponding ΔS_a values obtained are +0.0023, +0.0036, +0.004 and +0.0041 kJ/mol respectively. Similar values, -17 to -25 kJmol^{-1} for ΔG_a, -36 to -52 kJmol^{-1} for ΔH_a and -0.0657 to -0.0896 kJmol^{-1} for ΔS_a for n-heptane to n-decane, were reported by Dorris and Gray (1980) for thermomechanical pulp (TMP) fibres. The values

Table 3. ΔG_a (kJ.mol^{-1}), ΔH_a (kJK^{-1}.mol^{-1}) and ΔS_a (kJ.mol^{-1}) values calculated for the adsorption of n-alkanes hexane to decane on untreated, acid treated and solvent treated water hyacinth root biomass.

Biomass treatment	Alkane	ΔG_a	ΔH_a	ΔS_a
Untreated	n-Hexane	-20.422	-21.182	+0.0023
	n-Heptane	-29.546	-30.739	+0.0036
	n-Octane	-32.287	-33.621	+0.004
	n-Nonane	-44.439	-45.837	+0.0041
	n-Decane	-35.992	-33.704	+0.0071
Acid treated	n-Hexane	-38.521	-36.332	+0.0069
	n-Heptane	-38.793	-36.332	+0.0077
	n-Octane	-38.186	-35.935	+0.007
	n-Nonane	-36.077	-34.014	+0.0041
Solvent treated	n-Hexane	-40.980	-38.349	+0.0082
	n-Heptane	-39.303	-37.04	+0.0071
	n-Octane	-43.650	-40.988	+0.0083
	n-Nonane	-46.704	-43.704	+0.0094

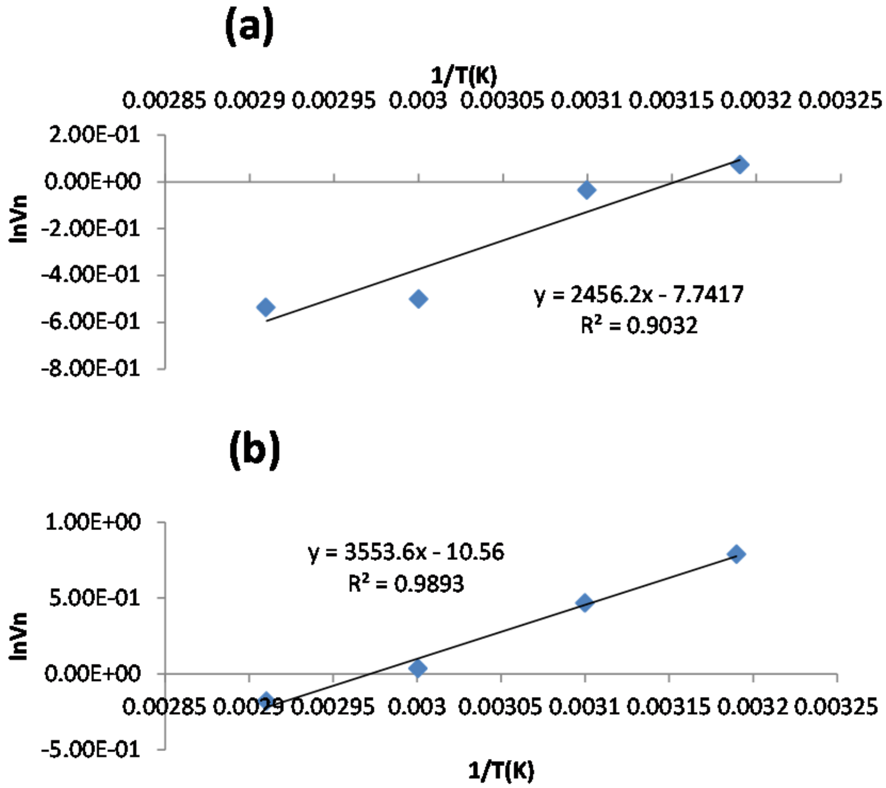

Figure 2. Plot of *$\ln V_n$* versus *1/T* for (a) n-hexane, (b) n-heptane for untreated water hyacinth root biomass.

obtained for ΔG_a. ΔH_a and ΔS_a show that adsorption occurs spontaneously and is exothermic, and involves very little entropy change. The little positive entropy change exhibited may be attributed to the slight change

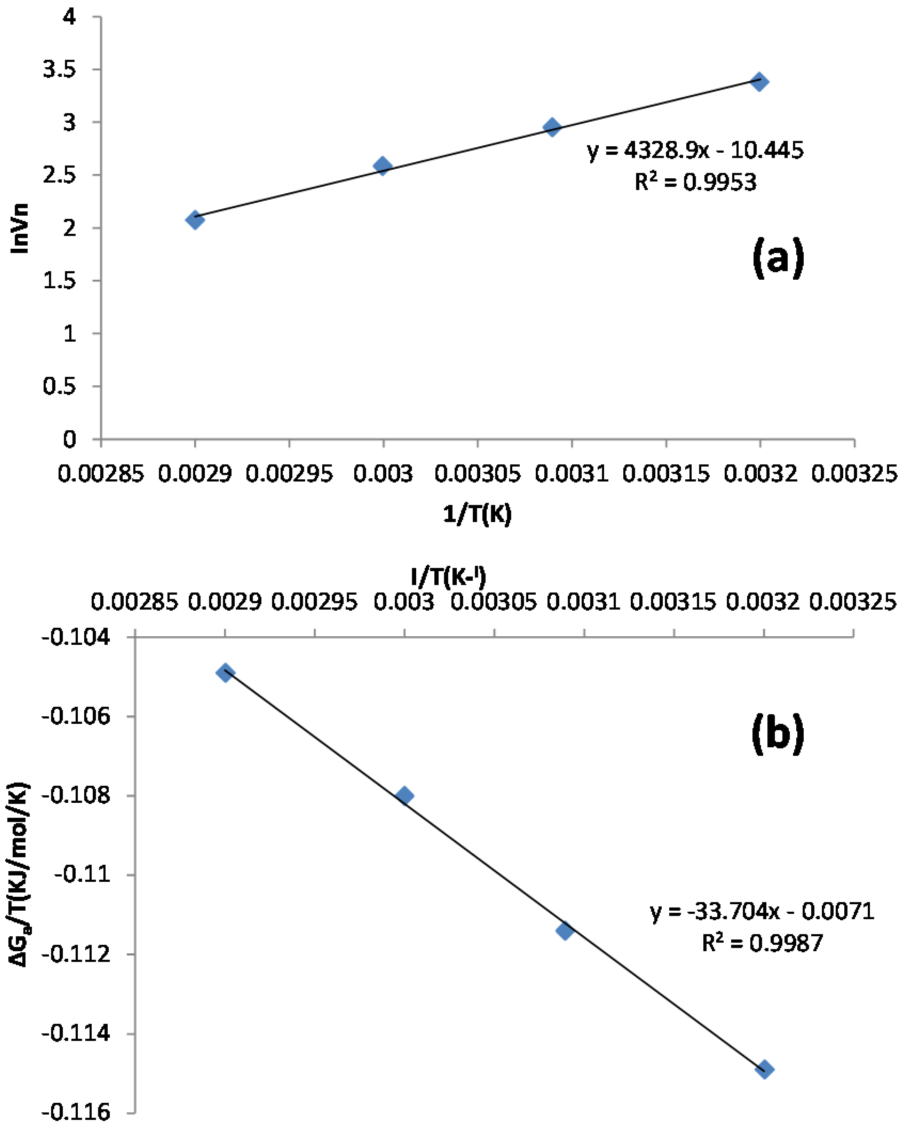

Figure 3. Plot of (a) *lnVn* versus *1/T* and (b) *ΔGa/T* versus *1/T* for n-decane on untreated water hyacinth root biomass.

in the volume of the stationary phase upon adsorption of the adsorbate.

Treated water hyacinth root biomass

Table 3 shows that higher -ΔG_a and -ΔH_a values, 36.077 to 38.783 kJ.mol^{-1} and 34.014 to 36.332 kJ.K^{-1}mol^{-1} respectively, were obtained for the acid treated water hyacinth root biomass samples, as compared to 20.442 to 35.992 kJ.mol^{-1} and 21.182 to 33.704 kJ.K^{-1}mol^{-1} respectively, for the untreated sample. Thus treatment of water hyacinth root biomass with dilute mineral acid leads to stronger adsorption bonds as compared to untreated water hyacinth root biomass. The increase in -ΔG_a and -ΔH_a upon dilute mineral acid treatment of water hyacinth root biomass is attributed to the hydrolysis of hemicelluloses. Hemicellulose molecules are normally H-bonded to cellulose. Hydrolysis must free O-H groups in the cellulose microfibrils for H-bonding with the n-alkane probes.

Tables 3 also shows that -ΔG_a and -ΔH_a values at 40.98 to 46.704 kJ.mol^{-1} and 38.349 to 43.704 kJ.K^{-1}mol^{-1}, respectively, for the solvent extracted water hyacinth root biomass, are higher than those for the acid treated water hyacinth root biomass, showing that organic solvent extraction leads to higher adsorption bond strength than obtained for both untreated and mineral acid treated water hyacinth root biomass. We attribute this increase in the adsorption bond to the removal of the protective waxy

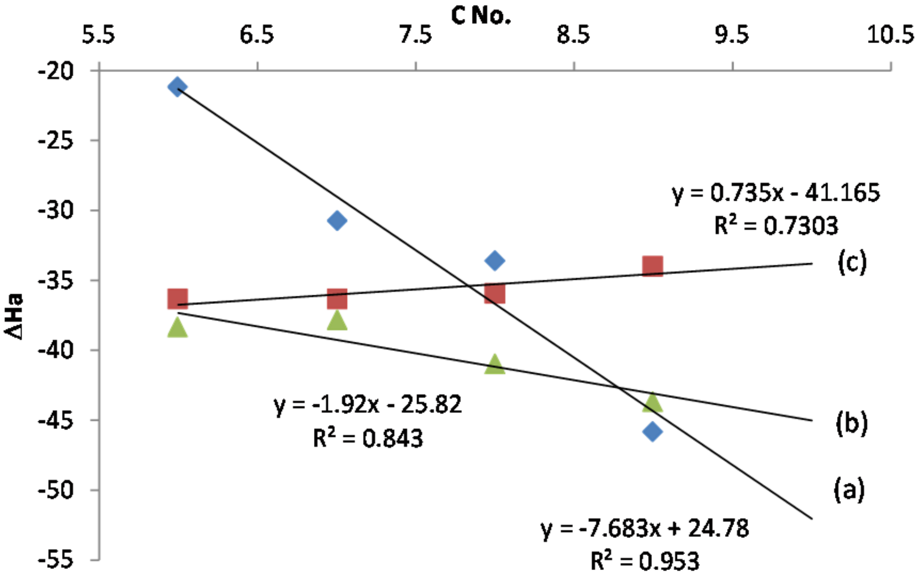

Figure 4. Plot of ΔH_a as a function of carbon number (C No.) for the adsorption of n-alkanes hexane to nonane on (a) untreated, (b) acid treated, and (c) solvent treated water hyacinth root biomass.

layer that normally covers the fibres, thereby deactivating the surface (Cordeiro et al., 2011a). Cordeiro et al. (2011a) have suggested that if extraction removes this waxy layer, a significant change in adsorption properties can be expected.

Figure 4 shows regression plots of ΔH_a as a function of n-alkane carbon number 6 to 9, for (a) untreated, (b) acid treated and (c) organic solvent treated water hyacinth root biomass. The regression curve for untreated root biomass is fairly linear with a slope of -7.683 and an R^2 value of 0.953. Linearity of ΔH_a with *C*-number has been reported previously for cellulose by Dorris and Gray (1980), who interpreted the slope of the ΔH_a versus *C*-number plot, of -5.3 kJmol^{-1}, as giving the enthalpy per *C*-centre or CH_2 group. Dorris and Gray (1980) concluded that the constant increment per CH_2 group in the enthalpy of adsorption was consistent with a flat orientation of the isolated n-alkane molecule on the surface of the cellulose fibres. Such an orientation permits maximum number of contact points with the adsorbent surface. Thus from Figure 4, the enthalpy for adsorption per CH_2 group is -7.683 kJmol^{-1} for untreated water hyacinth root biomass. The value of ΔH_a obtained by Doris and Gray (1980) suggests that contact occurs via the CH group orbitals and involves -5.3 kJmol^{-1} enthalpy, while the value of ΔH_a obtained in present study suggests that contact via CH_2 group orbitals involves -7.7 kJmol^{-1} enthalpy. Figure 5 shows that adsorption contact occurs via CH_2 group orbitals, which is consistent with a saw-tooth conformation or orientation of the n-alkanes on the surface of the water hyacinth root biomass adsorbent, whereas for the systems studied by Doris and Gray (1980), the alkanes assume the flat orientation in which contact occurs predominately via the CH group orbitals. It would appear that whether the n-alkane assumes the flat orientation or the saw-tooth orientation, depends on the physical properties of the adsorbent, such as particle size. Smaller particles result in a tighter column packing that would favour the flat orientation, while larger particles result in a looser packing that might favour the saw-tooth orientation.

Figure 5 shows very good agreement between the experimental ΔH_a value and that predicted from the $\Delta H_{a(CH2)}$ value for n-heptane. For n-hexane, n-octane and n-nonane, the experimental value deviates from that predicted on the basis of the $\Delta H_{a(CH2)}$ value by 8.7% respectively for n-hexane and n-octane, and 16.2% for n-nonane. We attribute the deviation, in the case of n-octane and n-nonane, to the a small fraction of molecules adsorbed in the flat orientation. The deviation of the experimental ΔH_a value from the predicted value for n-hexane can only be attributed to experimental error.

In Figure 4 the slopes of the regression curves for acid and solvent treated root biomass are -1.92 and 0.735, respectively. Since the experimental $-\Delta H_a$ values for the acid and solvent treated water hyacinth root biomass are much higher than those for the untreated biomass, regression slopes more negative than -7.683 are predicted if the n-alkane adsorbate assumes the flat or saw-tooth adsorption orientation.

The deviation of the experimental regression slopes from the predicted slopes can only be interpreted to mean that the n-alkane adsorbates do not assume the flat or saw-tooth adsorption orientation on the acid and

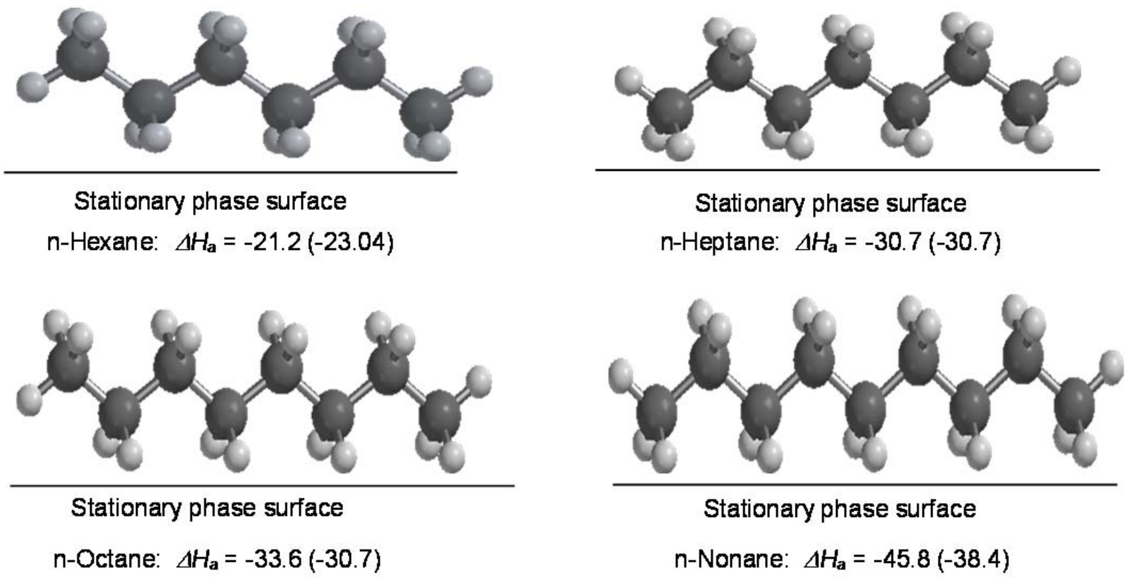

Figure 5. Adsorption of n-hexane, n-heptane, n-octane, and n-nonane by ground dried water hyacinth root biomass stationary phase during inverse gas chromatography: Possible conformation on solid phase stationary (ΔH_a = experimental value (predicted value); structures generated using the Spartan '08 V1.2.0 software, Wavefunction Inc., CA). SPS = Stationary phase surface.

Table 4. Regression coefficient (R^2) for the correlation of ΔH_a with water hyacinth root biomass powder surface area, pore volume and pore size.

N-alkane	Surface area	Pore volume	Pore size
n-Hexane	0.6673	0.1269	0.3371
n-Heptane	0.6037	0.1741	0.2762
n-Octane	0.9554	0.0014	0.7274
n-Nonane	0.1592	0.9747	0.4616

solvent treated root biomass.

Table 1 shows that nitric acid treatment increased the surface area and pore volume of the root biomass by 9.9 and 10.7% respectively, but had no effect on pore size. Organic solvent treatment on the other hand increased the surface area and pore size by 30 and 22.6%, respectively, but had no effect on pore volume. For n-hexane and n-heptane, Table 4 shows that the increase in ΔH_a correlates with the increase in surface area that result from acid and solvent treatment (R^2 values of 0.6673 and 0.6037, respectively). For n-octane, the increase in ΔH_a correlates with the increase in both surface area and pore size (R^2 values of 0.9554 and 0.7274, respectively), while for n-nonane, the increase in ΔH_a correlates with the increase in pore volume.

Enthalpy data for the adsorption of n-alkane hydrocarbons has been determined for a number of adsorbents. Widegren and Bruno (2011) determined the enthalpy for the adsorption of n-hexane, n-heptane and n-octane on concrete, synthetic clay Lonite-Rd and high purity kaolin, while Bilgic and Askin (2003) determined the enthalpy for the adsorption of n-hexane on molecular sieve 3A, molecular sieve 5A and alumina. ΔH_a values obtained are summarized in Table 5. Comparison of ΔH_a data in Table 5 to ΔH_a data obtained in the present study for the adsorption of n-alkanes by water hyacinth root biomass in Table 3 shows that the water hyacinth root biomass compares well with the molecular sieves 3A and 5A, and with alumina, especially after mineral acid and organic solvent treatment.

Conclusions

From the foregoing discussion, we conclude that the enthalpy of the adsorption of n-alkanes on water hyacinth root biomass is comparable to the enthalpy of the adsorption on molecular sieves 3A and 5A, as well as alumina. This makes water hyacinth root biomass a good adsorbent for n-alkane hydrocarbons. The strength of adsorption bond is also reflected in the very low values of the entropy of adsorption, +0.0023 to +0.0071 $kJ.mol^{-1}$, exhibited for the adsorption of n-alkanes by the material. Treatment of the material with dilute mineral acid or organic solvent improves the strength of the absorption bond significantly.

Conflict of interest

The authors did not declare any conflict of interest.

Table 5. Values of $-\Delta H_a$ ($kJK^{-1}mol^{-1}$) reported in the literature for the adsorption of hydrocarbons on concrete, synthetic clay, kaolin and molecular sieves 3A and 5A.

n-Alkane	**$-\Delta H_a$ ($kJK^{-1}mol^{-1}$)**					
	Concrete[a]	**Clay[a]**	**Kaolin[a]**	**3A[b]**	**5A[b]**	**Alumina[b]**
n-Hexane	34.3	56.0	59	27.5	34.7	41.0
n-Heptane	36.5	61.6	69			
n-Octane	42.0	65.2	81			

Source: [a]Widegren and Bruno, 2011; [b]Bilgic and Askin, 2003.

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