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ORIGINAL PAPER

Adsorption of volatile polar organic solvents on water hyacinth (*Eichhornia crassipes*) root biomass: thermodynamic parameters and mechanism

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Abstract The adsorbent properties of dried water hyacinth root biomass towards four polar solvents (dichloromethane, ethyl acetate, diethyl ether and acetone) were studied by inverse gas chromatography between 40 and 70 °C. The enthalpy of adsorption values obtained for the adsorption of the four solvents on untreated root biomass range from -51.234 kJ mol^{-1} for acetone, an amphoteric solvent, to -74.658 kJ mol^{-1} for dichloromethane, an acidic solvent. Mineral acid and organic solvent treatment led to reduction in the values of the enthalpy of adsorption for all four solvents. The Lewis acidity parameters calculated from the enthalpy of adsorption values were 0.408, 0.267 and 0.356, while the corresponding Lewis basicity parameters were 3.76, 1.80 and 2.34, respectively, for untreated, mineral acid-treated and organic solvent-treated water hyacinth root biomass. The Lewis basicity parameter-to-Lewis acidity parameter ratios for the untreated, acid-treated and organic solvent-treated biomass were found to be 9.22, 6.74 and 6.57, respectively, indicating (a) that all the surfaces of the untreated, mineral acid-treated and organic solvent-treated water hyacinth root biomass are basic in nature and (b) that for all volatile polar solvents studied, the adsorption interaction involves the lowest unoccupied molecular orbital of the solvent as the electron acceptor and the highest occupied molecular orbital of the water hyacinth root biomass surface adsorbent site as the electron donor.

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Keywords Biosorbent · Enthalpy of adsorption · Gas–solid chromatography · Inverse gas chromatography · Lewis acid–base properties

Introduction

Water hyacinth (*Eichhornia crassipes*) is a floating aquatic weed belonging to the pickerelweed family, *Pontederiaceae,* which is widely distributed throughout the tropics. It is found in India, Africa, South America, etc., and is considered one of the most productive and fastest growing plants on earth (Low et al. 1994; Martina et al. 2004; Mall et al. 2005; Rajamohan 2009). Water hyacinth can tolerate a wide variation in pH, temperature and nutrients (Rajamohan 2009), and it is therefore no wonder that water hyacinth, being renewable and readily available, has in recent years attracted the attention of scientists as a source of low-cost biomaterial for industrial use, including its use as a biosorbent (Rajamohan 2009). Zhou et al. (2009) reported that water hyacinth is composed of lignocellulosic fibres containing cellulose, hemicelluloses and lignin. 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. Hemicellulose is highly hydrophilic, partly soluble in water, soluble in alkalis and easily hydrolysed in acids (John and Thomas 2009; Spinace et al. 2009). Lignin is a complex three-dimensional hydrocarbon co-polymer of aliphatic and aromatic constituents of very high molecular weight. Lignin is completely amorphous, hydrophobic in nature and 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, i.e. whether it is from a leaf, bast, fruit or root. Recently, Mukaratirwa-Muchanyereyi et al. (2016) reported that the surface of water hyacinth root biomass is composed of several different functional groups which include aliphatic groups, carboxylates, aromatic and alcoholic moieties, and that dilute mineral acid and organic solvent treatment lead to changes in the surface composition and a reduction in the level of lignin in the biomass, which in turn leads to increased crystallinity and thermal stability of the root biomass.

The adsorbent properties of water hyacinth biomass towards heavy metals have been studied by several workers (Zaranyika and Ndapwadza 1995; Zheng et al. 2009; Hasan et al. 2010; Ibrahim et al. 2012; Mahamadi and Nharingo 2010a, b) and were recently reviewed by Mahamadi (2011) who concluded that water hyacinth biomass showed excellent biosorbent properties towards several heavy metals and that further investigations were required on the structural properties of the material before and after modification. The adsorbent properties of water hyacinth biomass towards organic dyes and phenols have also been studied. Thus, Tarawou et al. (2007) and Rajamohan (2009) studied the adsorption of methyl red and Congo red dyes by water hyacinth, while Khan et al. (2012) and El-Khalary (2007) studied the adsorption of methylene blue onto water hyacinth biomaterial, and Woverton and McKown (1976) studied the removal of phenols from polluted water using water hyacinth biomaterial as adsorbent. In a recent paper, Mukaratirwa-Muchanyereyi et al. (2015) reported on the effect of organic solvent and mineral acid treatment on the thermodynamic parameters for the adsorption of volatile n-alkane hydrocarbons n-hexane to n-decane, by water hyacinth root biomass, as typical examples of volatile non-polar organic air and water pollutants. The aim of the present paper was to study the thermodynamics and mechanism of the adsorption of acetone, diethyl ether, ethyl acetate and dichloromethane, by water hyacinth root biomass, as typical examples of volatile polar organic air and water pollutants. The solvents selected are produced and used in extremely large quantities by industry. Acetone is a skin and eye irritant, and long-term exposure can lead to dermatitis and may harm the nervous system (Canadian Centre for Occupational Health and Safety 2015). Dichloromethane is toxic if inhaled and is also a skin and eye irritant and a possible carcinogen (Canadian Centre for Occupational Health and Safety 2015). Diethyl ether is a harmful air pollutant that causes eye and respiratory tract irritation and can cause narcosis (NIOSH 2014). Ethyl acetate is a mild eye, nose and respiratory tract irritant that may cause mild narcosis at high concentrations (OSHA 2012).

The study was conducted at the University of Zimbabwe, Zimbabwe, during 2013–2015.

Theoretical

The adsorption of molecules of a liquid or gas on the surface of solids can be interpreted in terms acid–base interactions between the adsorbent surface and adsorbate molecules (Wypych 2001). In terms of the molecular orbital theory, a base is defined as a species that employs a doubly occupied orbital in initiating a reaction, while an acid is defined as a species that employs an empty orbital in initiating a reaction, i.e. the base is an electron donor, and the acid is the electron acceptor (Bistac and Brogly 2001). The donor orbital is usually the highest occupied molecular orbital (HOMO), and the acceptor orbital is usually the lowest unoccupied molecular orbital (LUMO). The extent of electron donation can range from essentially zero in the case of completely ionic interactions, to a complete transfer of one or both electrons from the donor to the acceptor. The donor number (DN) and acceptor number (AN) were introduced to give a quantitative measure of the extent of electron donation between the donor and acceptor, based on its interaction with a reference standard electron acceptor or electron donor (Gutmann 1977).

The DN number of a solvent is given by the enthalpy of its reaction with $SbCl_5$ as an arbitrarily chosen reference acid (Gutmann scale). The AN number is given by the ^{31}P NMR shift induced by triethylphosphine, again as an arbitrarily chosen reference base (Mayer 1979). On this scale, the AN number of hexane is zero, while that of $SbCl_5$ is 100. The AN number was later modified by Riddle and Fowkes (1990) to AN^*, expressed in energy units, similar to the DN number. The enthalpy of adsorption, ΔH_a, is a thermodynamic measure of the strength of the adsorption interaction (Widegren and Bruno 2011). In turn, ΔH_a is related to the AN and DN numbers by the equation (Wypych 2001):

$$\Delta H_a = K_a(\mathrm{DN}) + K_b(\mathrm{AN}) \quad (1)$$

where K_a and K_b are the acid and base interaction constants which characterise the acid and base properties of the adsorbent. Equation 1 shows that the plot of $\Delta H/\mathrm{AN}$ versus DN/AN is linear, with slope equal to K_a and intercept equal to K_b. The overall acid–base character of the biomass's surface can be evaluated from the K_b/K_a ratio (Ma et al. 2008). If $K_b/K_a > 1$, the surface is considered to be basic, meaning the surface of the solid prefers to donate electrons, while when $K_b/K_a < 1$, the surface is considered to be acidic (Ma et al. 2008; Cordeiro et al. 2011a; Santos et al. 2001). The AN, AN* and DN numbers for solvents commonly used in studying acid–base properties of sorbents are

Table 1 AN, AN* and DN numbers for solvents commonly used in studying thermodynamic properties of sorbents. *Source* Bistac and Brogly 2001; Zhao and Boluck 2010

Solvent	AN	AN* (kJ/mol)	DN (kJ/mol)	Specific characteristics
Acetone	12.5	10.5	71.2	Amphoteric
Water	54.8	63.2	75.3	Amphoteric
Ethyl acetate	9.3	6.3	71.6	Amphoteric
Dichloromethane	23.1	22.6	0	Acidic
Diethyl ether	3.9	5.89	80.40	Basic

available in the literature, see Table 1 (Bistac and Brogly 2001; Zhao and Boluck 2010).

ΔH_a is determined using inverse gas chromatography (IGC). IGC is gas solid chromatography (GSC) in which the adsorbent is employed as the stationary phase. IGC is an established method used for the determination of thermodynamic properties of sorbents. It can be shown that in GSC, the free energy of adsorption, ΔG_a, is related to the adsorbate retention volume by Eq. 2 (Cordeiro et al. 2011a; Kunaver et al. 2004):

$$\ln V_N = -\frac{\Delta G_a}{RT} + C \quad (2)$$

ΔG_a is a function of temperature from Eq. 3 (Voelkel et al. 2009):

$$\Delta G = \Delta H + T\Delta S \quad (3)$$

Hence

$$\ln V_N = -\frac{\Delta H_a}{RT} - \frac{\Delta S_a}{R} + C = -\frac{\Delta H_a}{RT} + C' \quad (4)$$

where

$$C' = C - \Delta S_a/R \quad (5)$$

Thus, a plot of $\ln V_N$ versus $1/T$ should yield a linear plot of slope $= -\Delta H_a/R$ and intercept $= C - \Delta S_a/R$. V_N is given by Eq. 6 (Laub and Pecsock 1978; Grob 1977):

$$V_N = \left(\frac{3}{2}\right) F \left(\frac{T}{T_a}\right)(t_R - t_M)\left\{\frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1}\right\} \quad (6)$$

where F = measured carrier gas flow rate, T = column temperature, T_a = ambient temperature, t_R = solute retention time, t_M = retention time of unretained solute, P_i = column inlet pressure and P_o = column outlet pressure.

Materials and methods

Equipment

A Varian 3400CX gas chromatograph equipped with a flame ionisation detector (Varian Chromatographic systems, Walnut Creek, California, USA) was used. The IGC experiments were carried out using a stainless steel column, 90 cm × 2.1 mm ID (Sigma-Aldrich, Germany) packed with 150–212 µm ground water hyacinth root biomass. High-purity nitrogen from a nitrogen gas generator (M4NT-1, Toyo Electric Ltd, Japan) was used as carrier gas. Sieves, 150 µm and 212 µm (BS410/1986, Endecots Ltd, London, England), were used to sieve the water hyacinth root biomass after grinding. A Hamilton GC syringe, 1.0 ml (Sigma-Aldrich, Germany), was used for the IGC injections.

Materials

Water hyacinth root biomass

Water hyacinth plants were collected from Waerera River, Bindura, Zimbabwe, at Universal Transverse Mercator(UTM) coordinate of (318500;8078400). At the laboratory, the plants were washed with tape water several times and then 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 and then sieved first through the 150-µm sieve and then through the 212-µm sieve.

Volatile polar organic solvents

Ethyl acetate (EA), acetone (AC), dichloromethane(DC) and diethyl ether (DE) (analytical grade, Sigma-Aldrich, Germany) were used as representative polar probes (Shi and Qi 2012; Kunavar et al. 2004). Methane (99.99 %, Fedgas, Johannesburg, South Africa) was used as the non-interacting probe (Cordeiro et al. 2011b).

Procedures

Solvent extraction of water hyacinth root biomass

Samples of the 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 (Tshabalala and Han 1999).

Acid treatment of water hyacinth root biomass

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).

Gas solid chromatography: determination of optimum flow rate

Preliminary experiments were run to establish the optimum N_2 carrier gas flow rate, by injecting 0.2 µL of octane at different carrier gas flow rates and noting the retention time (t_R) and the peak width at half-height ($w_{1/2}$) and then calculating the height equivalent of a theoretical plate (HETP), given by (Rouessac and Rouessac, 2007):

$$\mathrm{HETP} = \frac{L}{N} = \frac{L w_{1/2}^2}{5.5 t_R^2} \quad (7)$$

where L = column length and N = number of theoretical plates in the column at a given carrier gas flow rate. Plotting HETP versus flow rate yields the van Deemter curve. The optimum flow rate is given by the minimum in the van Deemter curve (Rouessac and Rouessac 2007) and was obtained as 6.4 ml min^{-1}.

Determination of specific retention volume (V_N) and the enthalpy of adsorption (ΔH_a)

IGC chromatograms were obtained for the volatile polar solvents acetone, diethyl ether, ethyl acetate and dichloromethane, under the following GC conditions: carrier gas flow rate, 6.4 ml/min; detector and injector temperature, 220 °C; and column temperature, isothermal at 40, 50, 60 and 70 °C. The column was conditioned for 2 h prior to injecting the volatile polar solvents. 0.2 µl of the solvent was injected each time. At least three injections were made for each solvent at each column temperature. Figure 1 shows typical chromatograms obtained for (a) diethyl ether at 40 °C and (b) ethyl acetate and (c) acetone at 70 °C. Table 2 shows the retention times obtained for ethyl

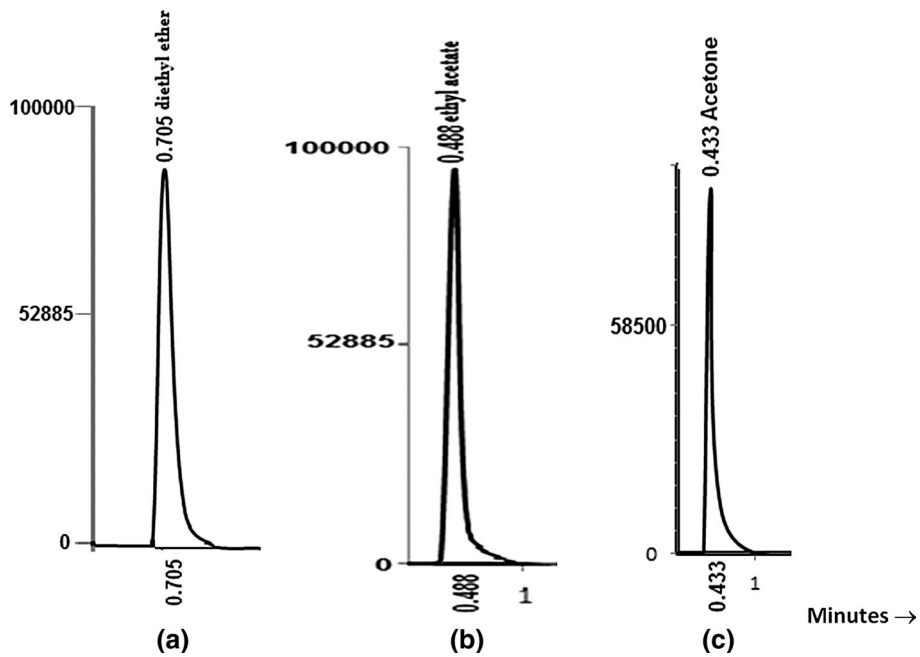

Fig. 1 Chromatogram of **a** diethyl ether at 40 °C, **b** ethyl acetate at 70 °C and **c** acetone at 70 °C, carrier gas flow rate = 6.4 ml/min

Table 2 Retention times (t_R) for diethyl ether, acetone, dichloromethane and ethyl acetate on untreated water hyacinth root biomass stationary phase

Temperature (°C)	t_R (min)			
	Diethyl ether	Acetone	Dichloromethane	Ethyl acetate
40	0.75 ± 0.00	0.83 ± 0.00	0.84 ± 0.01	1.15 ± 0.02
50	0.46 ± 0.06	0.46 ± 0.00	0.44 ± 0.00	0.56 ± 0.00
60	0.44 ± 0.00	0.45 ± 0.00	0.43 ± 0.27	0.53 ± 0.00
70	0.42 ± 0.00	0.45 ± 0.01	0.41 ± 0.00	0.48 ± 0.01

Table 3 Regression data for the ln V_N versus $1/T$ plots for untreated, mineral acid-treated and organic solvent-treated water hyacinth root biomass

Biomass treatment	Solvent	Slope (=$\Delta H_a/R$)*	Intercept	R^2
Untreated	Diethyl ether	7051.8	−22.662	0.8265
	Acetone	6162.1	−19.74	0.6614
	Dichloromethane	8979.3	−28.718	0.8005
	Ethyl acetate	6512.7	−20.156	0.8183
Acid-treated	Diethyl ether	2355.8	−6.9431	0.88
	Acetone	4516.4	−12.462	0.9934
	Dichloromethane	3007	−8.6603	0.9489
	Ethyl acetate	4950.5	−13.301	0.9829
Solvent-treated	Diethyl ether	5582.5	−17.83	0.9513
	Acetone	1824.6	−5.7508	0.9874
	Dichloromethane	7530.8	−24.525	0.9706
	Ethyl acetate	5703.9	−17.348	0.9934

* See Eq. 4; ΔH_a = enthalpy of adsorption; R = ideal gas constant

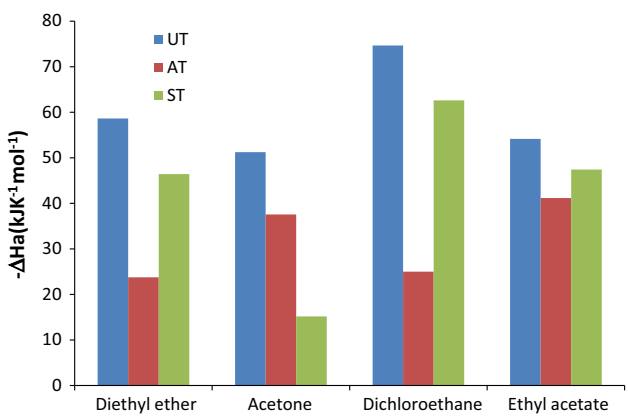

Fig. 2 Enthalpy of adsorption ($-\Delta H_a$) for diethyl ether, acetone, dichloromethane and ethyl acetate on untreated (UT), mineral acid-treated (AT) and organic solvent-treated (ST) water hyacinth root biomass

acetate, dichloromethane, acetone and diethyl ether on untreated water hyacinth root biomass. The ln V_N values were calculated and plotted as a function of $1/T$ (T = column temperature) for each solvent. Linear plots were obtained in each case, see Table 3. ΔH_a values calculated from the slopes of the ln V_N versus $1/T$ are shown in Fig. 2 in bar graph form.

Results and discussion

Adsorption thermodynamic parameters

Untreated water hyacinth root biomass

Figure 1 shows that sharp peaks were obtained for the volatile polar solvents at 70 °C column temperature and N_2 carrier gas flow rate of 6.4 ml/min. The retention data obtained (Table 2) show good reproducibility, with relative standard deviation in the range 0–13 %. Table 3 shows that the plot of ln V_N versus $1/T$ for all the volatile polar solvents used in the IGC experiments show good linearity (R^2 from 0.6614 to 0.9934), as predicted by Eq. 4. Enthalpy of adsorption ($-\Delta H_a$) for the volatile polar solvents, calculated from the slopes of the ln V_N versus $1/T$ plots, is shown in Fig. 2 in bar graph form. For untreated water hyacinth root biomass, the ΔH_a values of −58.632, −51.234, −74.658 and −54.149 kJ mol^{-1} were obtained for diethyl ether, acetone, dichloromethane and ethyl acetate, respectively. These values of $-\Delta H_a$ are comparable to values reported in the literature for different adsorbent materials, see Table 4, and show that adsorption is exothermic. For untreated water hyacinth root biomass, $-\Delta H_a$ values decrease in the order dichloromethane > diethyl ether > ethyl acetate > acetone.

Mineral acid-treated and organic solvent-treated water hyacinth root biomass

Figure 2 shows that mineral acid and organic solvent treatment leads to reduced values of $-\Delta H_a$ in all cases. Thus, for diethyl ether, acetone, dichloromethane and ethyl acetate, mineral acid treatment reduces $-\Delta H_a$ values by 59.5, 26.7, 66.5 and 24.0 %, respectively, while organic acid treatment reduces the values of $-\Delta H_a$ by 20.8, 70.4, 16.1 and 12.4 %, respectively. For diethyl ether, dichloromethane and ethyl acetate, the effect of mineral acid treatment on $-\Delta H_a$ is greater than that of organic solvent treatment. The reverse is true for acetone. Recently, Mukaratirwa-Muchanyereyi et al. (2015) reported that mineral acid and organic acid treatment leads to greater adsorption bond for n-alkane hydrocarbons. The conclusion from this is that adsorption on water hyacinth root biomass of n-alkane hydrocarbons and the volatile polar

Table 4 Values of $-\Delta H_a$ (kJ K^{-1} mol^{-1}) reported in the literature. *Source* [a] Askin and Yacizi 2005; [b] Fekete et al. 2004; [c] van Asten et al. 2000; [d] Onjia 2002; [e] Cordeiro et al. 2011a

Polar organic compound	$-\Delta H_a$ (kJ K^{-1} mol^{-1})					
	Sepiolite[a]	Calcium coated filler[b]	Twaron fibres[c]	$Na_2NiFe^{II}(CN)_6^d$	$Na_2NiFe^{II}(CN)_6^d$	Steam-treated fibres[e]
Acetone	29.23	–	51.7	–	–	–
Dichloromethane	40.58	–	39.2	–	–	–
Diethyl ether	–	38.5	6.6	–	–	–
Ethyl acetate	–	26.6	–	76.6	68.4	43.76

organic solvents under study involves different biomass surface groups. Whereas mineral acid and organic solvent treatment tends to reduce the biosorbent surface groups involved in the adsorption of the polar solvents, similar treatment tends to increase the surface groups involved in the adsorption of n-alkane hydrocarbons. As hemicellulose is easily hydrolysed by acids and lignin is not, this can only be explained by assuming that adsorption of n-alkanes occurs mostly on groups on, or directly linked to, the cellulose microfibrils and lignin. The adsorption of polar solvents, on the other hand, occurs on hemicellulose and other substances present in water hyacinth such as flavonoids, amino acids, phenols, proteins (Nyananyo et al. 2007; Rjiba et al. 2010).

Acid–base properties

The acid and base interaction constants, K_a and K_b, were determined according to Eq. 1. Figure 3 shows that plots of ΔH/AN versus DN/AN are fairly linear, $R^2 = 0.8286$, 0.6134 and 0.482, respectively, for (a) untreated, (b) acid-treated and (c) organic solvent-treated water hyacinth root biomass, from which the acid and base interaction constants K_a and K_b were obtained as 0.408 and 3.76, respectively, for the untreated, 0.267 and 1.80 for the acid-treated and 0.356 and 2.34 for the organic solvent-treated water hyacinth root biomass. Thus, solvent extraction and acid treatment reduced the basic character as well as the acidic character of water hyacinth root biomass.

The parameters K_a and K_b reflect the ability of the adsorbent surface to act as an electron acceptor and an electron donor, respectively. As discussed in the Theoretical section, if $K_b/K_a > 1$, the surface can be considered to be basic and therefore the electron donor, while if $K_b/K_a < 1$, the surface is the electron acceptor (Ma et al. 2008; Cordeiro et al. 2011a; Santos et al. 2001). The K_b/K_a ratios for the untreated, acid-treated and organic solvent-treated biomass were found to be 9.22, 6.74 and 6.57, respectively, indicating that all the surfaces of the untreated and treated biomass are basic in nature. This suggests that untreated, mineral acid-treated and organic solvent-treated water hyacinth root biomass possesses higher concentrations of

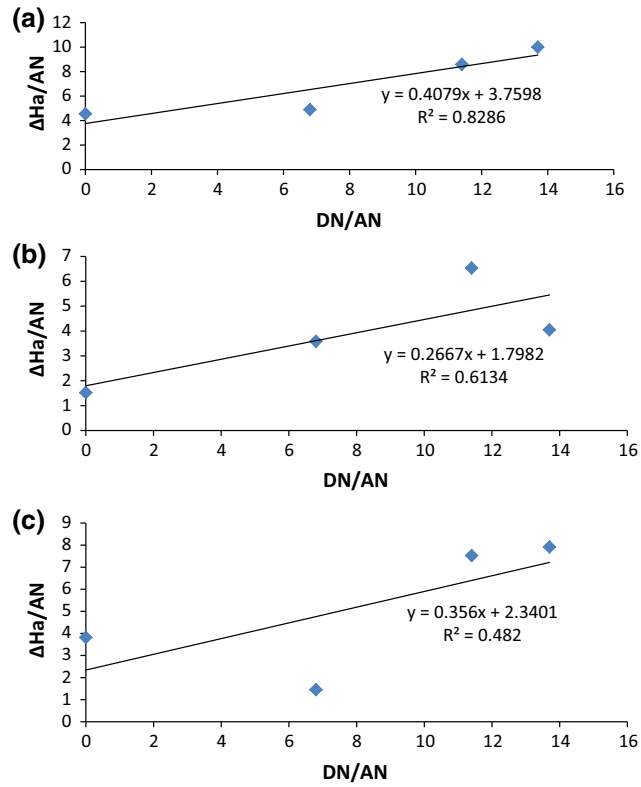

Fig. 3 Plot of ΔHa/AN versus DN/AN for **a** untreated, **b** acid-treated and **c** solvent-treated

electron-donating surface functional groups. Similar results were reported for most lignocellulosic materials that have been studied, see Table 5. Table 5 shows that most of the lignocellulosic materials that were studied exhibit basic properties, with $K_b > K_a$.

Cordeiro et al. (2011a, b) have shown that most natural fibre (e.g. flax, hemp, Kenaf, sisal, pineapple, Agave, assai, coir, silk floss jute, ramie, curana, pita Mexicana, piassava, sorghum) exhibit Lewis base character. Gannier and Glasser (1996) showed that the surface of cellulose is predominantly a Lewis acid in character and attributed this to the presence of surface hydroxyl groups, such that a high concentration of which renders the surface Lewis acidic, and therefore hydrophilic. The Lewis base character of

Table 5 Values of K_a and K_b values for non-wood fibres reported in the literature. *Source* (Gamelas 2013): K_a and K_b values were obtained from the ΔHa^s (specific enthalpy of adsorption) parameter (Mills et al. 2008; Heng et al. 2007; Mutuana et al.1998) or from the ΔGa^s (specific free energy of adsorption) at 25 °C (Cordeiro et al. 2011a)

Fibre	K_a	K_b	References
Wheat straw	0.15	0.79	Mills et al. (2008)
Wheat pulp bleached	0.10	0.47	Mills et al. (2008)
Rice hulls	0.21	0.38	Mills et al. (2008)
Reed	0.15	0.61	Mills et al. (2008)
Hemp	0.16	0.49	Mills et al. (2008)
	0.11	0.12	Heng et al. (2007)
	0.11	0.27	Cordeiro et al. (2011b)
Dichlorodiethylsilane-treated fibres	1.41	0.05	Mutuana et al.(1998)
Cellulose acetate propionate	0.41	1.71	Kuma et al. (2014)
Cellulose acetate butyrate	0.126	1.109	Kuma et al. (2014)

natural fibres has been attributed to low surface hydroxyl group concentration due to (a) inter- and intra-hydrogen bonding between hydroxyl groups, resulting in free ether linkages which could contribute to the basic character of the fibre, (b) the presence of lignin which exhibits a dominant basic character and (c) the presence of extractives like triglycerides which also exhibit basic character (Santos et al. 2001; Gulati and Sain. 2006).

Mechanism of adsorption

From the K_b/K_a ratios, we conclude that in molecular orbital theory terms, for each volatile polar solvent, the adsorption interaction involves the LUMO of the solvent as the electron acceptor, and the HOMO of the water hyacinth root biomass surface adsorbent site as the electron donor. Molecular orbitals for several organic molecules have been compiled by Jorgensen and Salem (1973). Acetone has 24 valence electrons, 12 filled orbitals and no half-filled orbitals. The LUMO is the $3B_1$ π^*_{CO} orbital at $E = 0.2996$ a.u. (E = energy; 1 a.u. = 27.21 eV). The LUMO for acetone, ethyl acetate, diethyl ether and dichloromethane is shown in Fig. 4. The orientations and conformations of the probes on the water hyacinth root biomass adsorbent particle surface shown in Fig. 4 were inferred from the LUMO to give optimum overlap with HOMO of electron-rich group on the adsorbent surface.

It is not possible to identify the electron-rich adsorbent sites on the surface of the water hyacinth root biomass adsorbent from the IGC data only. In Fig. 2, we note that mineral acid and organic solvent treatment leads to a reduction in the strength of the adsorption bond, suggesting that these adsorption sites are either removed or transformed by mineral acid and organic solvent treatment, more so by mineral acid in the case of diethyl ether, dichloromethane and ethyl acetate. The major component of lignocellulosic biomass that is affected by mineral acids is hemicelluloses. Hemicellulose molecules are highly hydrophilic, partly soluble in water, soluble in alkalis and easily hydrolysed by acids (John and Thomas 2009; Spinace et al.2009). Extraction with organic acids has also been reported to result in the removal of low molecular components at the surface of the fibre, such as fatty acids. Further work is underway in order to gain better insight into the nature of the electron-rich adsorbent sites on the surface of water hyacinth root biomass.

Effect of organic solvent polarity on adsorption bond strength

The overall polarity of organic molecules is measured in terms of its dipole moment, μ, in Debye units, and depends not only on the polarity of its individual bonds, but also upon the way the bonds are directed in space, i.e. upon the shape of the molecule. ΔH_a is a measure of the strength of the adsorption bond, and the more negative ΔH_a is, the stronger the adsorption bond. The plot of ΔH_a versus the solvent polarity, Fig. 5, shows that for untreated water hyacinth root biomass, negative but poor correlation exists between ΔH_a and the solvent polarity for the solvents under consideration. As discussed above, for the volatile solvents under study, adsorption involves the LUMO of the solvent. Polarity of molecules depends on the polarity of individual bonds, i.e. polarity is associated with the bonding electrons of individual bonds. Thus, poor correlation between ΔH_a and the solvent polarity is to be expected when adsorption involves the LUMO as is the case for the volatile solvents under study. As the adsorption interaction in this case involves overlap of the solvent LUMO and adsorbent surface donor group HOMO, we expect better correlation between ΔH_a and the difference in the energies of the solvent LUMO and surface adsorbent group HOMO, $\Delta E_{(LUMO/HOMO)}$.

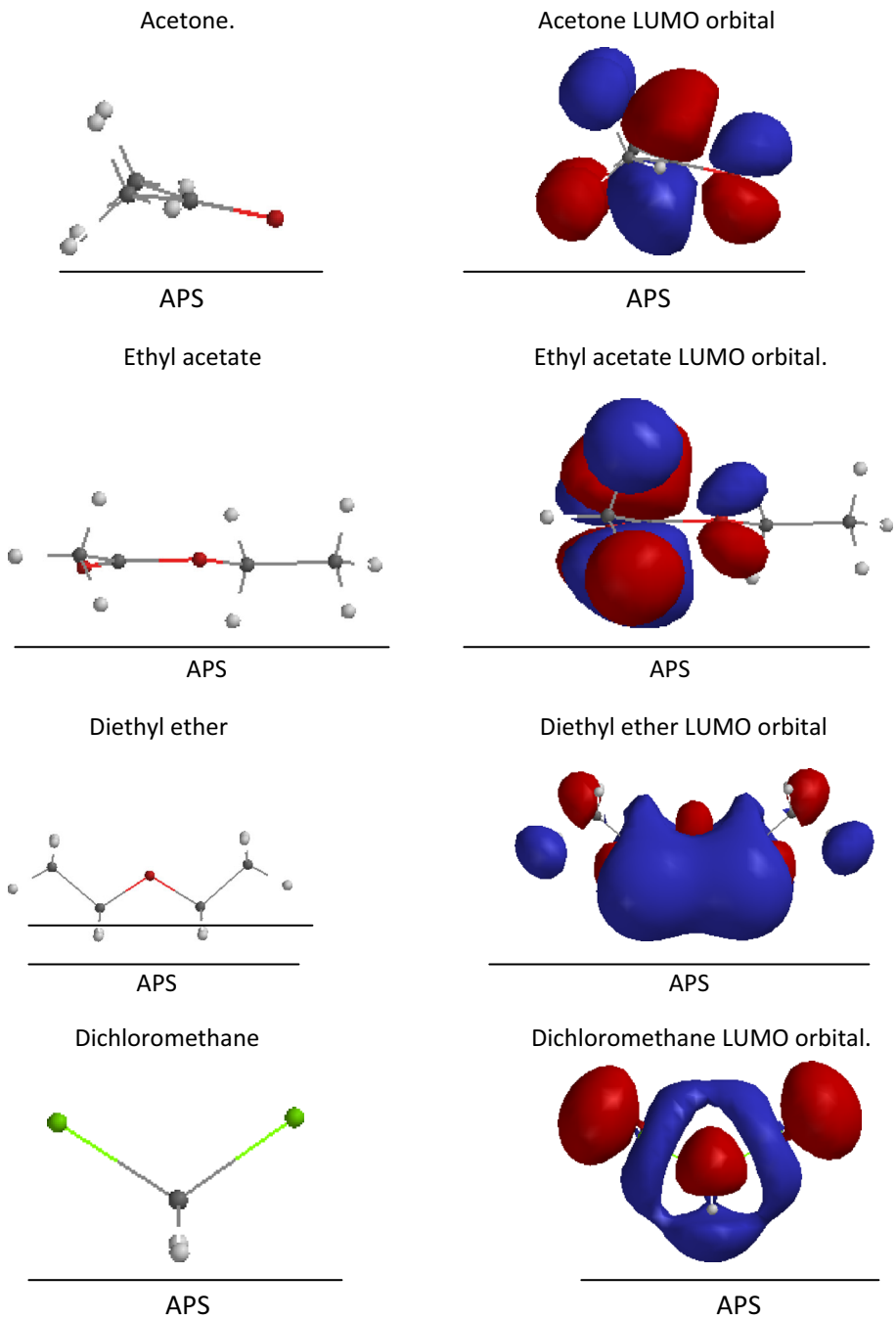

Fig. 4 LUMO and conformation of acetone, ethyl acetate, diethyl ether and dichloromethane on water hyacinth root biomass adsorbent particle surface (APS). (Structures generated using the Spartan'08 V1.20 software, Wavefunction Inc., CA)

Hudson and Klopman (1967) proposed an equation for the interaction energy (ΔE_{int}) to describe the effect of orbital perturbation upon the interaction of two molecules, thus (Bistac and Brogly 2001):

$$\Delta E_{\text{int}} = -\frac{Q_{\text{N}}Q_{\text{E}}}{\varepsilon R} + \frac{2(C_{\text{N}}C_{\text{E}}\beta)}{E_{\text{HOMO}} - E_{\text{LUMO}}} \quad (8)$$

where Q_{N} = total charges of nucleophile N, Q_{E} = total charges of electrophile E, C_{N} = coefficient of atomic orbital of nucleophile N, C_{E} = coefficient of atomic orbital of electrophile E, β = resonance integral, ε = permittivity, R = interatomic distance, and E_{HOMO} and E_{LUMO} denote the energy levels of the HOMO and LUMO of the interacting molecules. E_{int} is a sum of the electrostatic term and the electron donor–electron acceptor term. The first term dominates for electrostatic interactions, while the second term dominates for electron donor–electron acceptor interactions (Bistac and Brogly 2001). Thus, knowledge of both E_{HOMO} and E_{LUMO} is necessary in order to explain the trend in ΔH_{a} values, assuming that $\Delta E_{\text{int}} = \Delta H_{\text{a}}$ for adsorption interactions.

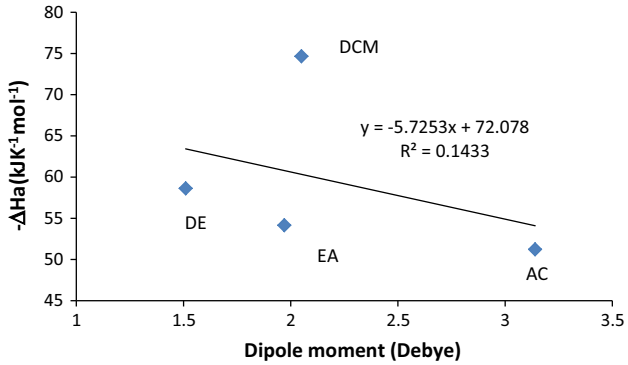

Fig. 5 Adsorption bond strength, $-\Delta H_a$, as a function of solvent polarity (*AC* acetone, *EA* ethyl acetate, *DE* diethyl ether and *DC* dichloromethane)

Conclusion

From the foregoing discussion, we conclude that the strength of the adsorption bond of volatile polar solvents on water hyacinth root biomass as represented by the enthalpy of adsorption is stronger than the adsorption bond with most lignocellulosic adsorbents that have previously been studied. This makes water hyacinth root biomass a good adsorbent for polar organic solvents. The negative ΔH suggests that the adsorption process is exothermic. The K_a and K_b parameters obtained for the water hyacinth root biomass suggest that the surface of dried water hyacinth root biomass is basic in character, and that adsorption of the polar solvents studied involves the LUMO of the solvent molecule. In addition, the Lewis basicity of the water hyacinth root biomass surface is reduced by mineral acid and organic solvent treatment, leading to reduced adsorption bond strength with the polar solvents.

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References

Askin A, Yacizi DT (2005) Surface characterization of sepiolite by inverse gas chromatography. Chromatographia 61(11–12):625–631

Bistac S, Brogly M (2001) Effect of polymer/solvent acid-base interactions: relevance to the aggregation of PMMA. In: Wypych G (ed) Handbook of solvents. ChemTech Publishing, Toronto

Canadian Centre for Occupational Health and Safety (2015) OSH answers fact sheets (a) Acetone, (b) Dichloromethane. Canadian Centre for Occupational Health and Safety, Ontario, Canada. www.ccohs.ca/oshanswers/chemicals/chem_profiles/….html. Accessed 7 Apr 2016

Cordeiro N, Gouveia C, John MJ (2011a) Investigating of surface properties of physic-chemically modified natural fibres using inverse gas chromatography. Ind Crops Prod 33:108–115

Cordeiro N, Gouveia C, Moraes AGO, Amico SC (2011b) Natural fibers characterization by inverse gas chromatography. Carbohydr Polym 84(1):110–117

El-Khalary MI (2007) Kinetics and mechanism of adsorption of methylene blue from aqueous solution by nitric acid treated water hyacinth. J Hazard Mater 147(1–2):28–36

Fekete E, Moczo J, Pukanszky B (2004) Determination of the surface characteristics of particulate fillers by inverse gas chromatography at infinite dilution: a critical approach. Colloid Interface Sci 269:143–152

Gamelas JAF (2013) The surface properties of cellulose and lignocellulosic materials assessed by inverse gas chromatography: a review. Cellulose 20(6):2675–2693

Garnier G, Glasser WG (1996) Measuring the surface energies of spherical cellulose beads by IGC. Polym Eng Sci 36(6):885–894

Grob RL (1977) Modern practice of gas chromatography. Wiley, New York, pp 21–30

Gulati D, Sain M (2006) Surface characteristics of untreated and modified hemp fibres. Polym Eng Sci 46(3):269–273

Gutmann V (1977) The donor-acceptor approach to molecular interaction. Plenum Press, New York

Hasan SH, Ranjan D, Talat M (2010) Water Hyacinth biomass (WHB) for the biosorption of hexavalent chromium: optimization of process parameters. Bioresources 5(2):563–575

Heng JYY, Pearse DF, Thielmann F, Lampke T, Bismarck A (2007) Methods to determine surface energies of natural fibers: a review. Compos Interface 14(7–9):581–604

Hudson RF, Klopman G (1967) A general treatment of chemical reactivity. Tetrahedron Lett 12:1103–1108

Ibrahim HS, Ammar NS, Soylak M, Ibrahim M (2012) Removal of Cd(II) and Pb(II) from aqueous solution using dried water hyacinth as a biosorbent. Spectrochim Acta A96:413–420

John M, Thomas S (2009) Biofibres and Biocomposites. Carbohydr Polym 71(3):343–364

Jorgensen ML, Salem L (1973) The organic chemists's book of orbitals. Academic Press, New York

Khan MR, Mozumder SI, Islam A, Prasad DMR, Alam MM (2012) Methylene blue adsorption onto water hyacinth: batch and column study. Water Air Soil Pollut 223(6):2943–2953

Kuma BP, Ramanaiah S, Reddy M, Reddy KS (2014) Surface characterization of cellulose acetate propionate by invers gas chromatography. Polym Bull 71(1):125–132

Kunaver M, Zadink J, Planinsck O, Srcic S (2004) Inverse gas chromatography—a different approach to characterization of solids and liquids. Acta Chim Slov 51(3):373–394

Laub RJ, Pecsock RL (1978) Physicochemical applications of gas chromatography. Wiley, New York

Low KS, Lee CK, Heng L (1994) Biosorption of basic dyes by *Hydrilla verticillata*. Environ Technol 15(2):115–124

Ma XY, Qu XH, Zhang Chen F (2008) Analysis of interfacial action of rectorite thermoplastic polyurethane nano composites by inverse gas chromatography and molecular simulation. Polymer 49(16):3590–3600

Mahamadi C (2011) Water hyacinth as a biosorbent: a review. Afr J Environ Sci Technol 5(13):1137–1145

Mahamadi C, Nharingo T (2010a) Utilization of water hyacinth weed (*Eichhornia Crassipes*) for the removal of Pb(II), Cd (II) and Zn (II) from aquatic environments: an adsorption isotherm study. Environ Technol 31(11):1221–1228

Mahamadi C, Nharingo T (2010b) Competitive adsorption of Pb(II), Cd(II) and Zn (II) ions onto *Eichhornia Crassipes* in Binary and Ternary systems. Bioresour Technol 101(3):859–864

Mall ID, Srivastava VC, Agarwal NK, Mishra IM (2005) Removal of congo red from aqueous solution by bagasse fly ash and activated carbon: kinetic study and equilibrium isotherm analysis. Chemosphere 61(4):492–501

Martina M, Jozefa F, Aleksander P (2004) Decoloration of the diazo dye reactive black 5 by immobilized Bjerkandera adusta in a stirred tank bioreactor. Acta Chim Slov 51(4):619–628

Mayer UA (1979) Semi empirical model for the description of solvent effects on chemical reactions. Pure Appl Chem 51(8):1697–1712

Mills RH, Gardner DJ, Wimmer R (2008) Inverse gas chromatography for determining the dispersive surface free energy and acid–base interactions of sheet molding compound-Part II 14 lignocellulosic fiber types for possible composite reinforcement. J Appl Polym Sci 110(6):3880–3888

Mukaratirwa-Muchanyereyi N, Kugara J, Zaranyika MF (2015) 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. Afr J Environ Sci Technol 9(3):282–291. doi:10.5897/AJEST2014.1817

Mukaratirwa-Muchanyereyi N, Kugara J, Zaranyika MF (2016) Surface composition and surface properties of water hyacinth (*Eichhornia crassipes*) root biomass: effect of mineral acid and organic solvent treatment. Afr J Biotechnol. 15(21):897–909. doi:10.5897/AJB2015.15068

Mutuana LM, Woodhams RT, Balatinecz JJ, Park CB (1998) Influence of interfacial interactions on the properties of PVC/Cellulosic fiber composites. Polym Comp 19(4):446–455

National Institute of Occupational Safety and Health (NIOSH) (2014) Diethyl ether. International Chemical Safety Card (ICSC): 0355. Centre for Disease Control and Prevention, US Department of Health and Human Resources, Atlanta, Georgia, USA. www.cdc.gov/niosh/ipcsneng/neng0355.html. Accessed 7 Apr 2016

Nyananyo BL, Gijo AH, Ogamba EN (2007) The physico-chemical distribution of water hyacinth (*Eichhornia crassipies*) on the river Nun in the Niger Delta. J Appl Sci Environ Manag 11(3):133–137

Occupational Safety and Health Administration (OSHA) (2012) Chemical Sampling Information: Ethyl Acetate. US Department of Labor, Occupational Safety and Health Administration, Washington, DC 20210. https://www.osha.gov/dts/chemicalsampling/data/CH_239500.html. Accessed 7 Apr 2016)

Onjia AE (2002) Inverse gas chromatography of chromia, part II. Finite surface coverage. J Serb Chem Soc 67(3):165–178

Rajamohan N (2009) Equilibrium studies on sorption of an anionic dye onto acid activated water hyacinth roots. Afr J Environ Sci Technol 3(11):399–404

Riddle FL Jr, Fawkes FM (1990) Spectral shifts in acid-base chemistry.1. van der Waals contributions to acceptor numbers. J Am Chem Soc 112(9):3259–3264

Rjiba N, Nardin M, Drean J, Frydrych R (2010) Comparison of surfaces properties of different types of cotton fibers by inverse gas chromatography. J Polym Res 17(1):25–32

Rouessac F, Rouessac A (2007) Chemical analysis. Modern instrumentation methods and techniques, vol 2. Wiley, West Sussex

Santos J, Gil MH, Portugal A, Guthrie J (2001) Characterization of cellulosic multi-purpose office paper by inverse gas chromatography. Cellulose 8(3):217–224

Shi B, Qi D (2012) A method for improving the calculation accuracy of acid base constants by inverse gas chromatography. J Chromatogr A 1231:73–76

Spinace MAS, Lambert CS, Fermoselli KKG, De Paoli MA (2009) Characterization of lignocellulosic curaua fibres. Carbohyd Polym 77(1):47–53

Tarawou T, Horsfall M Jr, Vicente JL (2007) Adsorption of methyl red by water hyacinth (*Eichhornia crassipes*). Biomass Chem Biodivers 4(9):2236–2245

Tshabalala MA, Han JS (1999) Effect of solvent extraction on surface energy of kenaf powder. In: Sellers T, Reichert NA (eds) Kenaf properties, processing and products. Mississippi State University, Mississippi, pp 121–131

van Asten A, van Veenendaal N, Koster S (2000) Surface characterization of industrial fibers with inverse gas chromatography. J Chromatography A 888(1):175–196

Voelkel A, Strzemiecka B, Adamska K, Milczewska K (2009) Inverse gas chromatography as a source of physicochemical data. J Chromatogr A 1216(10):1551–1566

Widegren JA, Bruno TJ (2011) Enthalpy of adsorption for hydrocarbons on concrete by inverse gas chromatography. J Chromatogr A 1218(28):4474–4477

Woverton BC, McKown MM (1976) Water Hyacinth for removal of phenols from polluted water. Aquat Bot 2:191–201

Wypych G (2001) General concept of acid-base interactions. In: Wypych G (ed) Handbook of solvents. Chemtech, Toronto

Zaranyika MF, Ndapwadza T (1995) Uptake of Ni Zn Fe Co Cr Pb, Cu and Cd by water hyacinth (*Eicchornia Crassipes*) in Mukuvisi and Manyame Rivers. Int J Environ Sci Health Part A Environ Sci Eng A 30(2):281–297

Zhao L, Boluck Y (2010) XPS and IGC characterization of steam treated triticale straw. Appl Surf Sci 257(1):180–185

Zheng JC, Feng HM, Lama MH, Lama PK, Ding YW, Yua HQ (2009) Removal of Cu (II) in aqueous media by biosorption using water hyacinth roots as a biosorbent material. J Hazard Mater 171(1–3):780–785

Zhou W, Zhu D, Langdon A, Li L, Liao S, Tan L (2009) The structure characterization of cellulose xanthogenate derived from the straw of *Eichhornia crassipes*. Bioresour Technol 100(21):5366–5369