

Full Length Research Paper

Surface composition and surface properties of water hyacinth (*Eichhornia crassipes*) root biomass: Effect of mineral acid and organic solvent treatment

Netai Mukaratirwa-Muchanyereyi^{1,2}, Jameson Kugara¹ and Mark Fungayi Zaranyika^{1*}¹Chemistry Department, University of Zimbabwe, P. O. Box MP 167 Mount Pleasant, Harare, Zimbabwe.²Bindura University of Science Education, Bindura, Zimbabwe.

Received 26 October, 2015; Accepted 11 March, 2016

The surface composition and surface properties of water hyacinth (*Eichhornia crassipes*) root biomass were studied before and after extraction with dilute nitric acid and toluene/ethanol (2/1, v/v) followed by ethanol, using Fourier Transform Infra-red (FT-IR) spectroscopy, thermogravimetric analysis, x-ray diffraction, scanning electron microscopy. FT-IR absorption bands were obtained at 3421, 2855, 1457 and 1035 cm^{-1} (O-H stretch, C-H vibration, C-H asymmetric deformation, and C-O stretch, respectively) and 1508, 1541 and 1559 cm^{-1} (all aromatic skeletal vibrations characteristic of lignin), as well as a C=O carboxylate stretch vibrational band at 1654 cm^{-1} . Scanning electron microscopy confirmed the root biomass to be amorphous and not to have a strongly structured surface. The dilute mineral acid and organic solvent treatment increased crystallinity. Thermogravimetric analysis Studies show that the treated biomass are more thermally stable than the untreated biomass. Data are presented showing that dilute mineral acid and organic solvent treatment resulted in a decrease in the amount of lignin in the biomass. The implications of the decrease in the percentage of lignin on the adsorption of volatile polar organic solvents and non-polar n-alkane hydrocarbons is discussed.

Key words: Water hyacinth, biomass, surface composition, Fourier Transform Infra-red (FT-IR) spectroscopy, scanning electron microscopy, x-ray diffraction spectroscopy, thermo gravimetric analysis.

INTRODUCTION

The use of lignocellulosic biomaterials as adsorbents for various types of inorganic and organic water pollutants has been reviewed by Gupta et al. (2009), Mahamadi (2011), Hubbe et al. (2014), Priya et al. (2014) and Tran et al. (2015). The interest in bio-sorbents derives from the fact that biomaterials are environment friendly and are

readily available, and therefore qualify as low-cost adsorbents. Adsorbent properties of lignocellulosic materials depend on the plant type from which they are derived, the conditions under which the plant grew, the origin of the fibre (that is, whether root, rhizome, stem or leaf), particle size, surface composition, and any physical

*Corresponding author. E-mail: zaranyika@science.uz.ac.zw

or chemical pre-treatment the material is subjected to. Lignocellulosic biomaterials are composed of fibres that can be considered as naturally occurring composites, consisting mainly of helically wound cellulose microfibrils bound together by lignin and hemicelluloses. Cellulose is the most abundantly occurring natural polymer. Regardless of its source, cellulose is a polymer of β -D glucose units. The monomer units are linked together by α -(1-4)-glycosidic bonds forming straight chains. Each monomer has three hydroxyl groups. These chains are linked by hydrogen bonds as hydroxyl groups of the glucose units on one chain are able to form hydrogen bonds with an oxygen atom on the other chain. This enables the chains to be held together firmly to form microfibrils in which highly ordered (crystalline) regions exist with less ordered amorphous region (Celik and Demirbas, 2005).

Lignin is the second largest in abundance after cellulose. Unlike cellulose, lignin is a highly branched polyphenolic polymer that is three dimensional. It consists of three monomers namely p-coumaric alcohol, coniferyl alcohol and sinapyl alcohols. These are found in lignin as phenylpropane units (Martone et al., 2009). Lignin is located in the spaces between cellulose and hemicelluloses and pectin components in plant cell wall, and gives the plant cell wall mechanical strength. The percentage of lignin differs from one plant to another. In soft wood and hardwood, it forms 23 to 33% and 16 to 25% respectively of the total mass, whereas it forms 26 to 33% of the total mass in plant biomass (Miretzky and Cirelli, 2010). Lignins differ in terms of the degree of carbon-carbon crosslinking between phenyl groups (Celik and Demirbas, 2005). In hardwood it is covalently linked with xylans whereas in softwood it's linked with galactogluconanans. The chemical composition and physical composition of lignin depends on the method of isolation employed to separate it from the polysaccharide moieties. The common functional groups in lignin include aliphatic and phenolic hydroxyl groups (9 to 11%), methoxy groups (13 to 26%), and carbonyl groups (Miretzky and Cirelli, 2010).

Hemicelluloses are short chain polymers of about 200 monosaccharide units composed of glucose, xylose, mannose, galactose, rhamnose, and arabinose. Hemicelluloses and cellulose are bound to lignin by hydrogen bonds (Miretzky and Cirelli, 2010). Lignocellulosic materials thus have carboxyl and hydroxyl functional groups that can be modified by chemical treatment to improve the selectivity of the adsorption (Bandosz, 2006). The available acidic and basic functional groups can be added or eliminated from the surface, thus governing the adsorption of either polar or non-polar species.

One plant that is receiving considerable attention as a potential low-cost bio-sorbent is water hyacinth (*Eichhornia crassipes*). Water hyacinth is a floating aquatic weed belonging to the pickerel weed family, *Pontederiaceae*. It is one of the fastest growing plants, and can tolerate a

considerable variation in nutrients, temperature and pH (Rezania et al., 2015). It has flourishing roots composed mainly of cellulose and lignin (Zheng et al., 2009). It has been investigated extensively for the removal of dyes from aqueous solution (Tarawou et al., 2007; Low et al., 1995; Rajamohan, 2009; Aboul-Fetoula et al., 2010; Saltabas et al., 2012; Khan et al., 2012; El-Khalary, 2007; Modenes et al., 2013; Mahamadi and Mawere, 2013; Uddin et al., 2013; Rajamohan et al., 2013; Kaur et al., 2013; Nath et al., 2014). Water hyacinth has also been investigated for the removal of phenols from polluted water by Woverton and McKown (1976). The adsorbent properties of water hyacinth biomass were recently reviewed by Priya et al. (2014) and Mahamadi (2011), who concluded that water hyacinth biomass showed excellent biosorbent properties, and that further investigations were required on the structural properties of the material before and after modification. The aim of the present study was to evaluate the effect of dilute mineral acid and organic solvent treatment on the surface chemistry and surface properties of water hyacinth root biomass. This was achieved by studying the surface composition and surface properties of the ground dried water hyacinth root biomass powder before and after extraction with dilute mineral acid (nitric acid) and an organic solvent mixture (toluene/ethanol, 2/1v/v, followed by ethanol), using Fourier Transform Infra-red (FT-IR) spectroscopy, thermo gravimetric analysis (TGA), x-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic absorption spectrometry (for elemental composition), in addition to standard chemical and physical methods for moisture, mineral matter (or ash), organic matter, organic carbon and lignin content determination.

MATERIALS AND METHODS

Equipment

A DR-8001 Shimadzu FT-IR Spectrophotometer (Shimadzu Corporation, Japan) was used for infrared characterization of the water hyacinth root biomass. A Bruker D2 Phase diffractometer (Bruker (Pvt) Ltd, Karlsruhe, Germany) X-ray was used to record diffractograms (XRD) of ground dried water hyacinth roots. A Jeol 6510 (Jeol, USA) Scanning Electron Microscope was used to obtain the SEM micrograms. A 6200 flame atomic absorption spectrometer (Shimadzu Corporation, Japan) was used for measuring the elemental composition for the root biomass. Sieves, 150 and 212 μ m (BS410/1986, Endecotts Ltd, London, England) were used to sieve the water hyacinth root biomass after grinding.

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 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, and then sieved first through the 212 μ m sieve, and

Table 1. Chemical composition of water hyacinth root biomass.

Variables	% MC ^a	%DM ^b	%MM ^c	%OM ^d	%OC ^e
Untreated	0.04±0.00	99.96±0.02	18.43±0.02	81.57±0.02	47.31±0.00
Nitric acid Treated	9.36±0.00	90.64±0.00	17.49±0.00	82.49±0.00	47.84±0.00
Organic solvent treated	0.057±0.00	99.94±0.03	17.41±0.03	82.59±0.03	47.90±0.00

^aMoisture content; ^bdry matter; ^cmineral matter or ash content, ^dorganic matter; ^eorganic carbon.

Table 2. %Lignin in Water Hyacinth root biomass.

%Lignin			References
Untreated	Acid treated	Solvent treated	
23	20	17	This study
27.7			Girisuta et al., 2008
9.93			Poddar et al., 1991
9.27			Abdelhamid, 1991
26.36			Chanakya et al.,1996
3.5			Nigam, 2002
15.2			Mukherjee and Nandi, 2004
12.2			Ahn et al., 2012
5.3			Fileto-Perez et al., 2013

then the 150 µm sieve, retaining the 150 to 212 µm fraction. Potassium bromide (AR grade, Sigma -Aldrich, Germany) was used to prepare KBr pellets for FT-IR analysis.

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 (Tshabalala and Han, 1999). 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

The water hyacinth root biomass powder was acid washed by soaking in 0.1 M HNO₃ for 24 h, followed by washing with deionized water, and drying at 65°C for 24 h.

Mineral matter, organic matter and organic carbon determination

About 1.0 g of the oven-dried samples was ashed in a muffle furnace at 550°C for 8 h. The ash was weighed to determine the amount of ash or mineral matter in the sample. The percentage of organic matter and organic carbon was determined using the following equations.

$$\%MM = \left(\frac{AW}{DW} \right) 100 \quad 1$$

$$\%OM = \left(\frac{DW - AW}{DW} \right) 100 \quad 2$$

$$\%OC = (\%OM)/1.724 \quad 3$$

Where, MM is mineral matter or ash, OM is organic matter, OC is organic carbon, AW is ash weight of the sample, DW is dry weight of the sample, and 1.724 is the van Bemmelen factor (that is, organic matter contains 58% OC) (Armecin and Gabon, 2008). The results obtained are shown in Table 1.

Lignin content determination

The amount of lignin in the untreated water hyacinth biomass and the treated water hyacinth root biomass was calculated from the remaining solid after the hydrolysis of the water hyacinth root biomass with 1.25% H₂SO₄ for 2 h followed by 72% H₂SO₄ for 4 h. The residues obtained were filtered and then washed with Distilled water in order to remove the sulphuric acid. The residues were then dried at 105°C to constant weight. The lignin in the samples was calculated using Equation 4 (Irfan et al., 2011).

$$\text{Lignin}\% = \frac{\text{LigninWeight}(g) \times 100}{\text{BiomassWeight}(g)} \quad 4$$

The results obtained are shown in Table 2.

Elemental composition

Approximately 0.5 g of the ground water hyacinth root biomass were weighed into a 100 ml Teflon beaker and digested with a

Table 3. Elemental analysis of untreated and acid treated biomass.

Element	Analysis ($\mu\text{g/g}$)		% Removal
	Before acid washing	After acid washing	
Fe	2399.2 \pm 0.2	317.9 \pm 0.01	86.8
Ni	172.4 \pm 0.3	42.95 \pm 0.00	75.1
Cu	427.3 \pm 0.1	205.4 \pm 0.02	51.9
Pb	176.6 \pm 0.1	163.8 \pm 0.9	7.2
Cr	244.66 \pm 0.03	52.6 \pm 0.1	78.5
Zn	616.5 \pm 0.6	154.3 \pm 0.1	75.0

mixture of 1 ml of 65% perchloric acid, 5 ml of 55% nitric acid and 0.5 ml 98% sulphuric acid, all GR grade, Merck, Germany. Heating was continued until the volume was reduced to approximately 2 ml, before transferring to a 100 ml volumetric flask, and diluting to the mark with deionised water for analysis by flame atomic absorption spectrometry (Muramoto et al., 1989). The levels of Fe, Ni, Cu, Pb, Cr and Zn in the root biomass were determined before and after acid treatment. The results obtained are shown in Table 3.

FT-IR spectrophotometry

Transmission mode FT-IR spectra of the KBr pellets of ground water hyacinth root biomass were obtained within the 4000 to 400 cm^{-1} wave number range at 4 cm^{-1} resolution. 50 scans were run for each sample and averaged. Figure 4 shows the FT-IR spectra obtained.

Thermal gravimetric analysis (TGA)

Thermal characteristics of the natural and treated samples were studied using TGA (STA 6000, Perkin Elmer, Massachusetts, USA) at a range of 34 to 900°C in a nitrogen atmosphere at a heating rate of 20°C/min. The data for derivative of the thermogravimetric analysis were also obtained from the same instrument and was used to plot derivative thermogravimetric analysis curves (DTA) (Figures 2 and 3).

X-Ray diffraction (XRD) and scanning electron microscopy (SEM) analysis

X-ray diffractograms (XRD) of ground dried water hyacinth roots were recorded in a Brucker D2 Phase diffractometer (Brucker (Pvt) Ltd, Karlsruhe, Germany) using 30 kV, 10 mA and $\text{CuK } \alpha$ -radiation, a step size of 0.01°, and a step scan of 1.05 s were used for the entire reading range (10 to 65°). Figure 4 shows the XRD spectra obtained. The SEM micrograms were obtained using a Jeol 6510 (Jeol, USA) Scanning Electron Microscope. The samples were clamped in such a way that they were presented to the analysing beam. Figures 5 and 6 show the typical SEM microgram obtained.

RESULTS AND DISCUSSION

Effect of mineral acid and organic solvent treatment on the chemical composition of water hyacinth root biomass

Table 3 shows the elemental composition of the roots of

water hyacinth from Waerera River, Bindura, Zimbabwe, before and after mineral acid treatment. Data for untreated water hyacinth root biomass was found to be 2399, 172, 427, 177, 245, and 617 $\mu\text{g/g}$ for Fe, Ni, Cu, Pb, Cr and Zn, respectively. The data in Table 3 shows that up to 86.8, 78.5, 75.1, 75, 51.9 and 7% of Fe, Cr, Ni, Zn, Cu and Pb respectively can be removed by soaking the water hyacinth root powder in 0.1 M nitric acid for 24 h, followed by washing with deionized water, and oven drying at 65°C for 24 h. Thus, while acid washing does not remove any of the metals completely, Fe, Ni, Cu, Cr and Zn are removed to a greater extent than Pb, suggesting that the major portions of Fe, Ni, Cu, Cr and Zn are loosely bound in the root biomass while the greater portion of Pb is more strongly bound.

The ash content of untreated, mineral acid treated and organic acid treated water hyacinth root biomass was found to be 18.43, 17.49 and 17.41 respectively (Table 2). Abdelhamid and Gabr (1991) reported an ash content of 27.7, Poddar et al. (1991) reported 16.29% and Patel et al. (1993) 20.2% for water hyacinth. An ash content of 7.91% was reported by Carvalho et al. (2015) for straw. The reduction in the ash content for the mineral acid treated biomass is in agreement with elemental analysis data for the acid treated sample which show that heavy metal content decreased after acid treatment (Table 3). Organic solvent treatment also caused a 5.5% reduction in the mineral content, most probably as a result of removal of extractable metal organic complexes in the water hyacinth root biomass.

The lignin content for the untreated, acid treated and organic solvent treated root biomass was found to be 23, 20 and 17% respectively. These values are within the range of those reported in literature for water hyacinth (Table 2). The lignin content of water hyacinth has been found to vary from 3 to 28% (Ahn et al., 2012), while land plants can have 20 to 40% hemicelluloses, 30 to 50 cellulose and 15 to 30% lignin (Bhattacharya and Kumar, 2010). Table 2 shows that organic solvent and mineral acid treatment lead to a reduction in the lignin content of 26 and 13% respectively.

Table 4 summarizes the peaks observed in the FT-IR spectra of untreated water hyacinth root biomass. The bands at 3691.62 and 3400 cm^{-1} are attributed to O-H

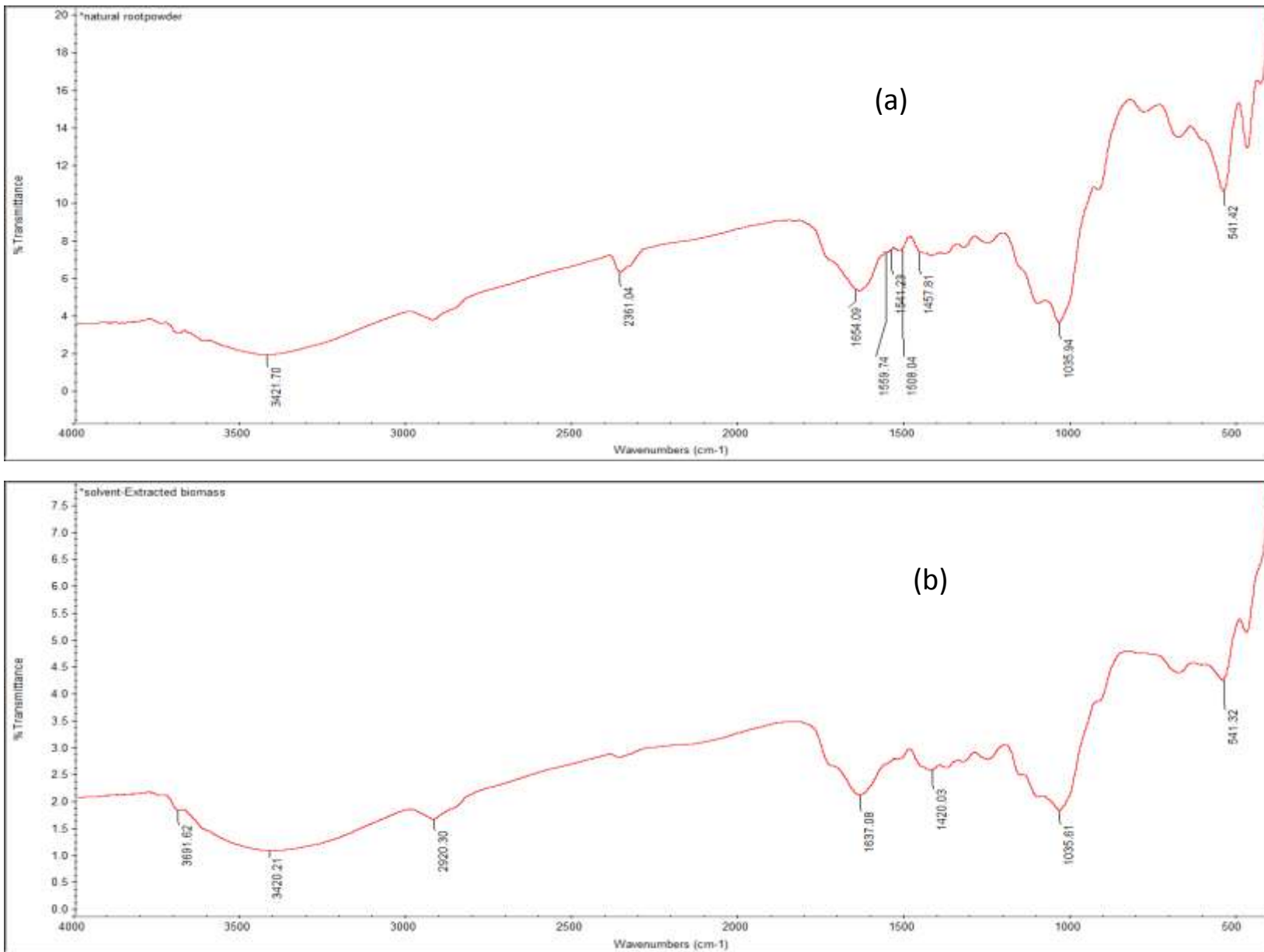


Figure 1. FTIR Spectra of (a) Natural, (b) solvent extracted, and (c) acid- treated water hyacinth biomass.

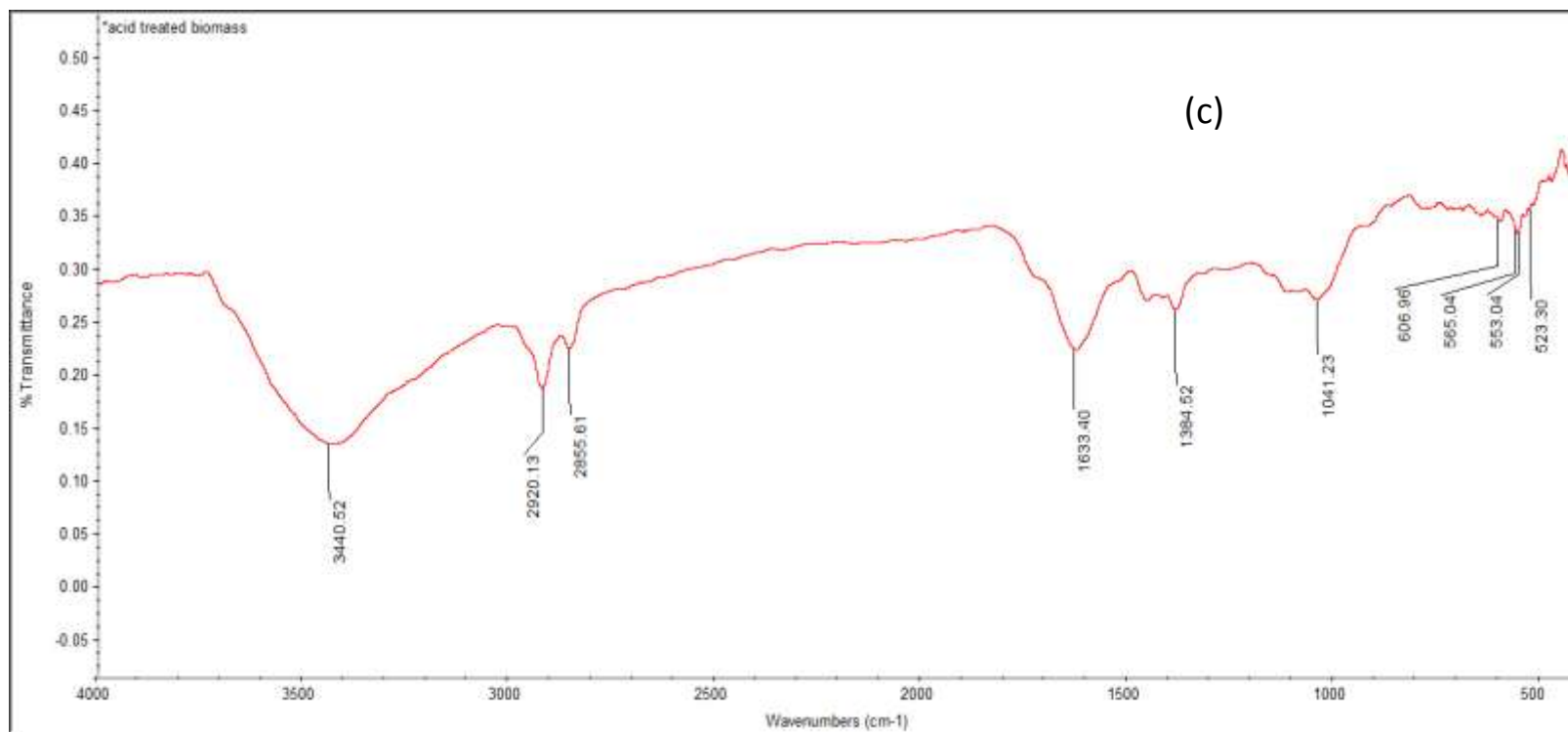


Figure 1. Contd.

stretch vibration (Sundari and Ramesh, 2012; Parikh, 1974). The band at 2920.30 cm^{-1} is attributed to C-H vibration for alkanes (Liu et al., 2006). The band at 2361.04 cm^{-1} was probably due to P-H or C=N (Parikh, 1974). The root biomass also shows a band at 1654.09 cm^{-1} attributed to C=O stretch vibration of carboxylate (Tshabalala et al., 2005; Liu et al., 2006; Southichak et al., 2006). Sundari and Ramesh (2012) reported a similar peak on water hyacinth nanofibers. The bands between 1500 cm^{-1} and 1600 cm^{-1} are attributed to the C=C aromatic

skeletal vibration of lignin (Cordeiro et al., 2011a). The bands at 1457.81 and 1035.94 cm^{-1} are attributed to C-H deformation and C-O stretch respectively (Tshabalala et al., 2005). The presence of C-O stretch indicates the presence of alcoholic hydroxyl groups (Lim et al., 2008). FT-IR data thus suggest that the water hyacinth root biomass is mainly lignocellulosic in composition.

The FT-IR spectrum shows that untreated water hyacinth root biomass contains a greater percentage of cellulose than lignin or hemicelluloses. This is demonstrated by the fact that the most

intense bands in the FT-IR of untreated water hyacinth root biomass are 3421.70 , 2920 and 1035.94 cm^{-1} attributed to O-H and C-H stretch vibrations typical of cellulose (Cordeiro et al., 2011a).

FT-IR bands: Effect of acid washing and solvent extraction

The peak at 3691.62 cm^{-1} , O-H stretch, was present in the solvent extracted water hyacinth root biomass

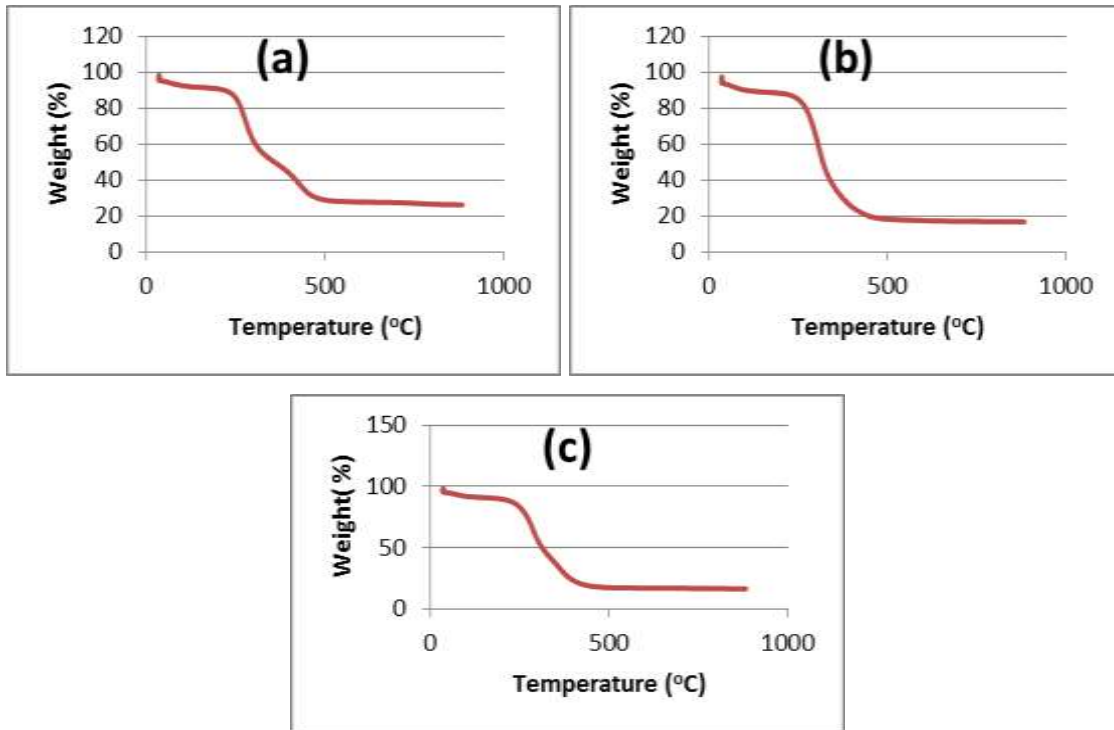


Figure 2. TGA thermogram of (a) untreated (b) solvent extracted, and (c) nitric acid treated water hyacinth (*Eichhornia crassipes*) root biomass.

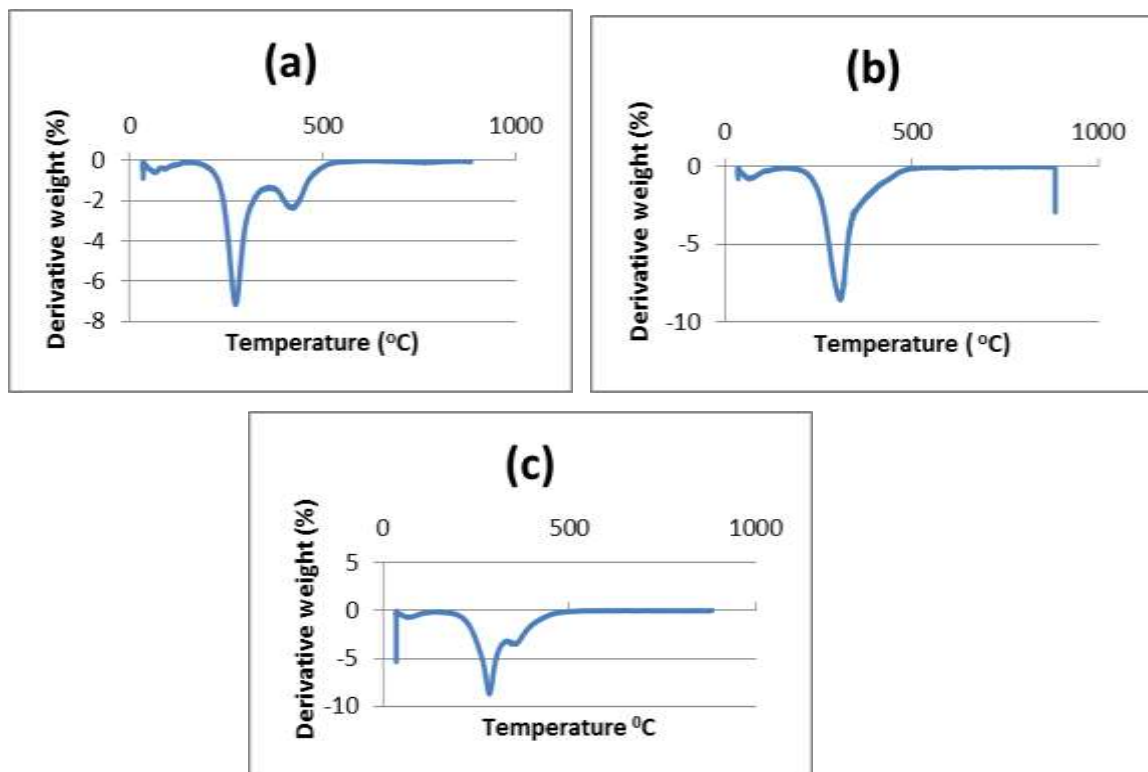


Figure 3. DTA curve for (a) untreated, (b) solvent treated, and (c) acid treated water hyacinth (*Eichhornia crassipes*) root biomass.

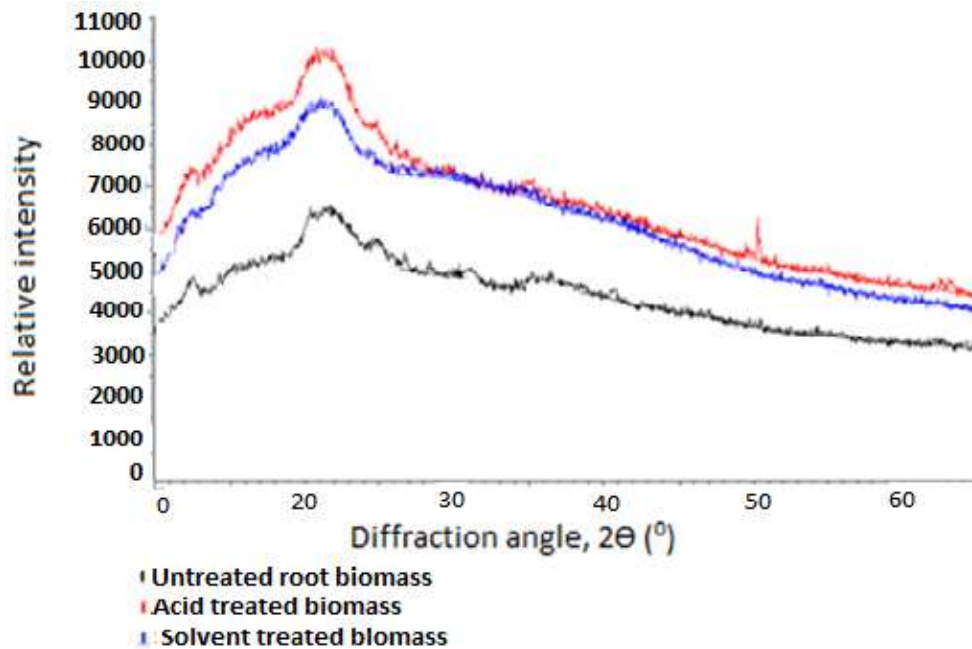


Figure 4. XRD diffractogram of ground dried water hyacinth (*Eicchornia crassipes*) untreated, acid treated and solvent extracted root biomass.

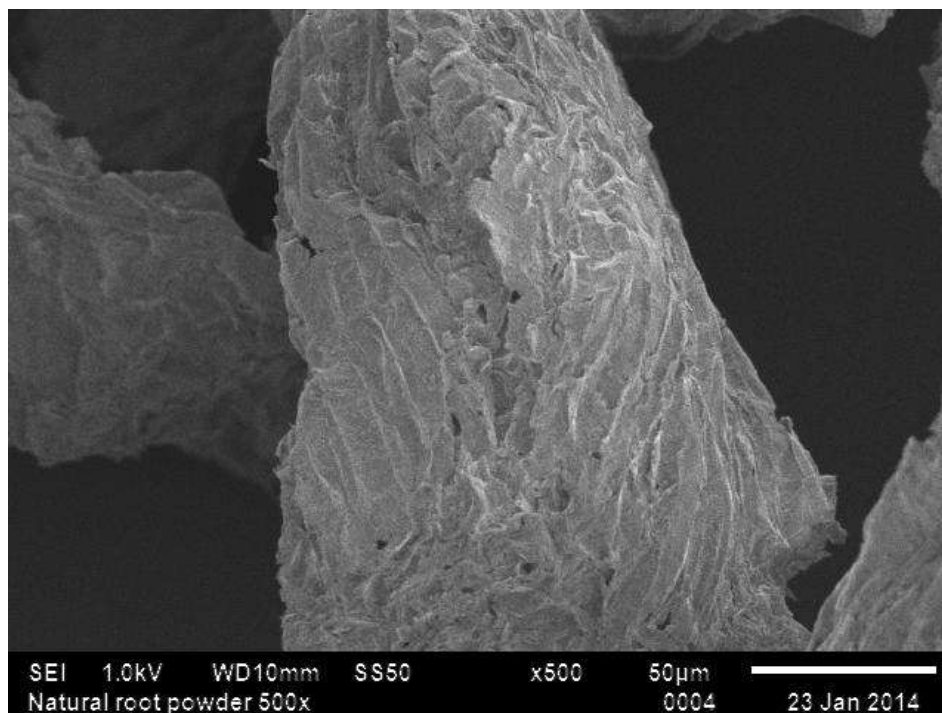


Figure 5. Scanning electron microscopy (SEM) microgram of untreated ground dried water hyacinth (*Eicchornia crassipes*) root biomass.

sample, but was absent in the acid washed sample. Both solvent extracted and acid washed samples show the

peak at 3420.70 cm^{-1} , O-H stretch vibration (bonded), although the peak for the solvent extracted sample is

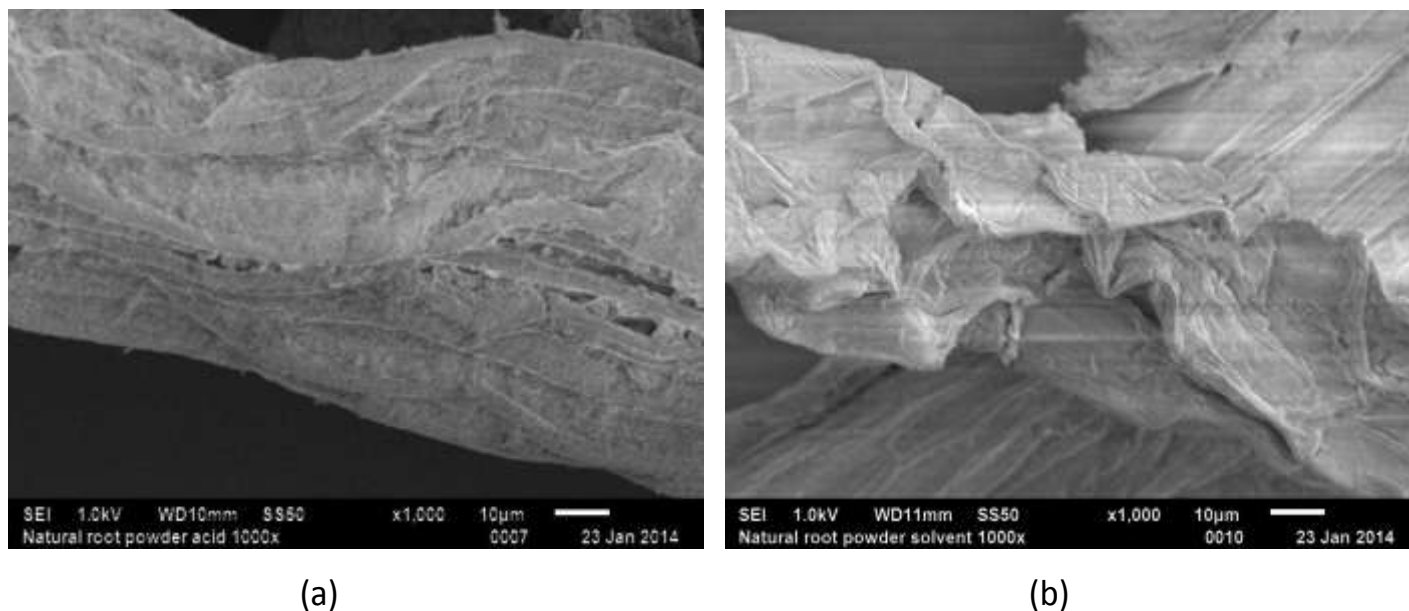


Figure 6. Scanning Electron Microscopy (SEM) microgram of ground dried water hyacinth (*Eicchornia crassipes*) root biomass: (a) acid treated; (b) solvent-extracted.

slightly shifted to higher energy at 3420.21 cm^{-1} , while that for acid washed sample is shifted downwards to 3440.52 cm^{-1} . The band at 2920.30 cm^{-1} , C-H vibration, is also present in both samples, but with a slight high energy shift to 2920.30 cm^{-1} . On the other hand, the band at 2361.04 cm^{-1} , was present in the solvent extracted sample, but absent in the acid washed sample. The loss of this peak in the acid washed sample was however accompanied by the appearance of a new peak at 2856.61 cm^{-1} . We attribute this new peak to C-H stretch (Parikh, 1974). The band at 1654.09 cm^{-1} , attributed to asymmetric and symmetric C-H stretch of the aliphatic groups (Parikh, 1974), is present in both mineral acid and organic solvent treated samples. The solvent extracted had a peak at 1637.08 cm^{-1} due to C=C and possibly adsorbed water. Peaks around that value are also due to C=O stretch vibration of carboxylate (Tshabalala et al., 2005; Liu et al., 2006; Southichak et al., 2006). The natural and the acid treated water hyacinth root biomass also showed the presence of the C=O stretch. Sundari and Ramesh (2012) reported a similar peak on the water hyacinth nanofibers (2012). Peaks between 1500 cm^{-1} and 1600 cm^{-1} are for the C=C aromatic skeletal vibration of lignin (Cordeiro et al., 2011a). These were observed in the natural biomass but not in the treated samples, suggesting that in the treated samples some lignin was removed by the treatment process. Peaks for C-H, as well as for C-O stretch, deformation was observed in all the samples (Tshabalala et al., 2005). The presence of C-O stretch indicates the presence of alcoholic hydroxyl groups (Lim et al., 2008). A summary of the peaks observed is shown in Table 4.

X-Ray diffraction and scanning electron microscopy analysis

In all the samples, Figure 4, there is a peak around the 22° reflection which corresponds to the (200) crystallographic plane (Tserki et al., 2005). A shoulder at around 16° is probably due to one of the 100 or $(1\bar{0}0)$ planes (Thiebaud and Borredon, 1995). For materials that have high cellulose content like cotton, flax or other fibers, one may observe two peaks around 16° , but in cases where the content of amorphous materials such as lignin, hemicelluloses and amorphous cellulose is high, the two peaks are smeared and may appear as one shoulder. Thus the appearance of one peak at 16° in all the XRD diffractograms for the water hyacinth root biomass samples, suggests the presence of a high content of such amorphous materials in untreated, mineral acid treated and organic acid treated water hyacinth root biomass. The relative intensities of the peaks for the treated samples are higher than for the untreated sample suggesting the treatment procedures increased the crystallinity of the biomass. This could be as a result of removal of some amorphous constituents of the root biomass during treatment. Zafeiropoulos et al. (2002) reported a similar increase in crystallinity after acetylation of flax fiber. Similarly, Cordeiro et al. (2011b) reported an increase in crystallinity for sisal fiber after alkaline treatment.

The SEM microgram, Figure 5, shows that the root powder does not have a thick epicuticular wax layer and it does not have a strongly structured surface, in agreement with the XRD results. The organic solvent and

Table 4. Summary of FT-IR bands in untreated water hyacinth root biomass.

Band (cm ⁻¹)	Assignment	References
3691.62	O-H stretch, alcohols	Parikh, 1974
3421.70	O-H stretch, alcohols	Tshabalala et al., 2005
2920.30	C-H vibration; alkanes.	Liu et al., 2006; Tahir and Alam, 2014.
2361.04	KBr	Tahir and Alam, 2014
1654.09	C=O stretch, carboxylate; KBr	Southichak et al., 2006
1559.74	C=O carbonyl	Parikh, 1974
1541.23	C=C aromatic skeletal vibration of lignin	Cordeiro et al. 2011a
	C=N stretching.	Parikh, 1974; Gouveia et al., 2009
	C=C Aromatic skeletal vibration of lignin	Cordeiro et al., 2011a
	C=N; C-N amides;	
1508.04	C=C Aromatic skeletal vibration of lignin; lignin ester	Parikh, 1974; Cordeiro et al 2011a; Southchak et al., 2006.
1457.81	C-H deformation assymmetric	Cordeiro et al., 2011a
1035.94	C-O Stretch	Lim et al., 2008

mineral acid treatment caused partial disintegration of the surface probably due to removal of part of hemicelluloses and lignin that interconnects the cellulose fibrils (Figures 5 and 6).

Thermogravimetric analysis

The initial loss in mass in the TGA curves (Figure 2, 50 to 200°C) is due to loss of adsorbed moisture in the water hyacinth root biomass. The residues that remain in untreated and treated biomass after 500°C constitute carbonaceous materials. The treatment increased the stability of the biomass. From the DTA curves (Figure 3), the main decomposition temperatures for the untreated, acid treated and organic solvent treated were found to be 270, 282.96 and 301.14°C respectively. The lower decomposition temperature for the untreated biomass probably is due to the presence of higher content of pectin, lignin and hemicelluloses which have lower decomposition temperature (Chen et al., 2011). The decomposition of the polymer structure of lignin start at low temperature of 200 to 600°C (Brebun and Vasile, 2010; Kubo and Kadla, 2008).

Effect of surface composition on adsorbent properties

Recently, Mukaratirwa-Muchanyereyi et al. (2015) reported that the enthalpy of adsorption of volatile n-alkane hydrocarbons (n-hexane to n-decane) by water hyacinth root biomass increases following dilute mineral acid or organic solvent treatment, whereas that for volatile polar organic solvents (diethyl ether, dichloro-methane, acetone, ethyl acetate) increases after similar treatment. Figure 7 shows the correlation of enthalpy for the adsorption of the volatile polar solvents on water hyacinth root biomass and

% lignin of the root biomass. All the plots show negative slope suggesting there is a positive correlation between enthalpy of adsorption and % lignin in the root biomass. Mukaratirwa-Muchanyereyi et al. (2015) attributed the decrease in the enthalpy of adsorption following mineral acid and organic solvent treatment to the removal of lignin and hemicelluloses on treatment. This interpretation is consistent with the trend in Figure 7. On the basis of these results we conclude that the adsorption of polar solvents by water hyacinth root biomass occurs mainly on lignin functional groups. For the adsorption of non-polar n-alkanes n-hexane, n-heptane and n-octane (Figure 8), the opposite trend is observed, suggesting negative correlation between enthalpy of adsorption and % lignin. The regression curves for n-hexane, n-heptane and n-octane show high linearity, with R² values of 0.8368, 0.8331 and 0.956 respectively. The increase in the enthalpy of following mineral acid and organic solvent treatment, suggests that the adsorption of the three n-alkanes by water hyacinth root biomass occurs mainly on cellulose chains. N-nonane shows a very low negative correlation coefficient (R² = 0.0286), suggesting little or no correlation between enthalpy of adsorption and % lignin for n-nonane.

Conclusions

From the foregoing discussion we conclude that the surface of the water hyacinth root biomass is composed of several different functional groups which include aliphatic groups, carboxylates, aromatic and alcoholic moieties. Dilute mineral acid and organic solvent treatment lead to, not only changes in the surface composition, but also a reduction in the level of lignin in the biomass, with the consequential increase in crystallinity and thermal stability of the biomass.

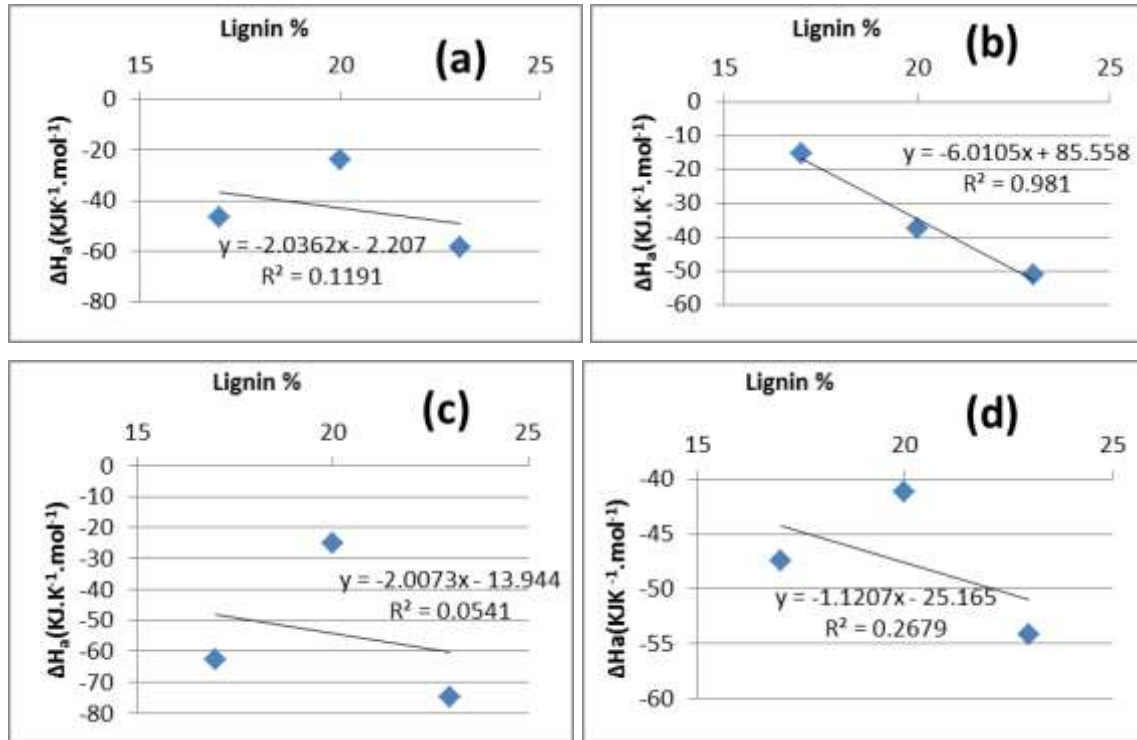


Figure 7. Plot of ΔH_a versus % lignin in water hyacinth root biomass: (a) Diethyl ether, (b) acetone, (C) dichloromethane and (d) ethyl acetate.

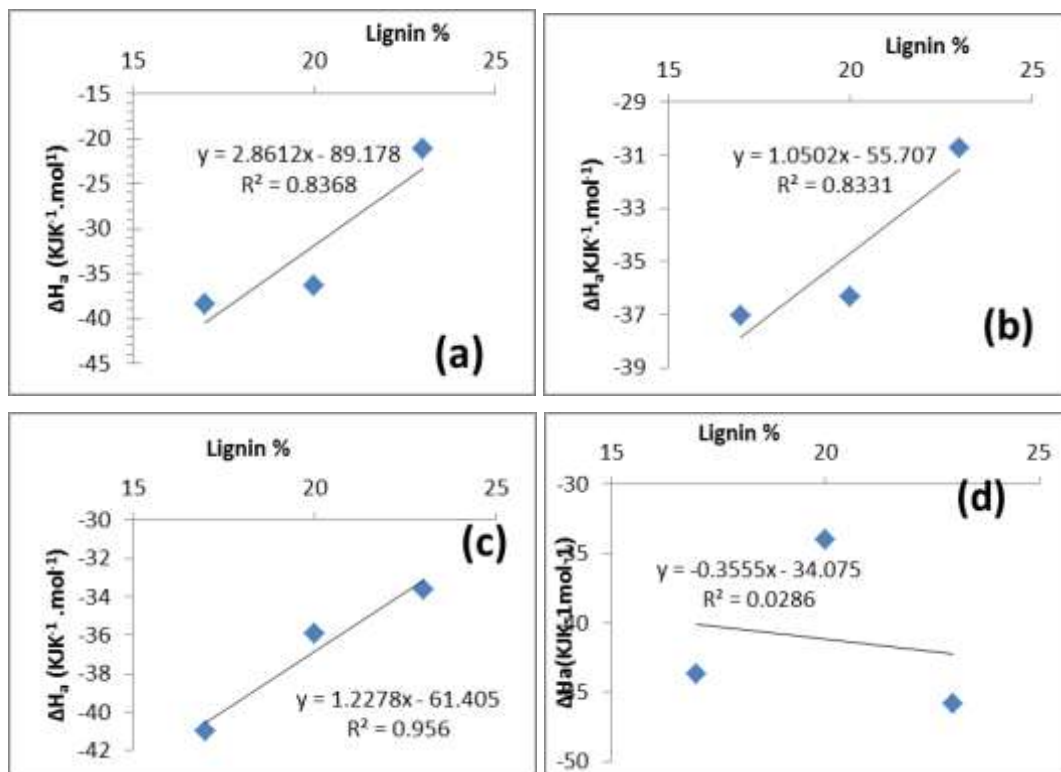


Figure 8. Plot of ΔH_a versus lignin percentage in the biomass a) Hexane b) Heptane c) Octane, d) Nonane.

Conflict of Interests

The authors have not declared any conflict of interests.

REFERENCES

- Aboul-Fetouh MS, Elmorsi TM, El-Kady JM, El-Adawi HA (2010). Water hyacinth stems: a potential natural adsorbent for the adsorption of acid green 20 dye. *Environ. Sci.* 5:257-266.
- Ahn DJ, Kim SE, Yan HS (2012). Optimization of pretreatment and Saccharification for production of bioethanol from WHC by *Saccharomyces cerevisiae*. *Bioprocess. Biosyst.* 35:35-41.
- Armecin RB, Gabon FM (2008). Biomass, organic carbon and mineral matter contents of abaca (*Musa textilis* Nee) at different stages of growth. *Ind. Crop Prod.* 28:340-345.
- Bandosz TJ (2006). Activated carbon surfaces in environmental remediation. Academic Press.
- Bhattacharya A, Kumar P (2010). Water hyacinth as a potential biofuel crop. *Electron. J. Environ. Agric. Food Chem.* 9(1):112-122.
- Brebu M, Vasile C (2010). Thermal degradation of lignin: A review. *Cellulose Chem. Technol.* 44(9):353-363.
- Celik A, Demirbas A (2005) Removal of heavy metal ions from aqueous solutions via adsorption onto modified lignin from pulping wastes. *Energy Sources* 27(12): 1167-1177. DOI: 10.1080/00908310490479583.
- Chanakya HN, Borgaonkar S, Meena G, Jagadish KS (1996). Solid phase biogas production with garbage or water hyacinth. *Bioresour. Technol.* 46:227-231.
- Chen W, Yu H, Liu Y, Hai Y, Zhang M, Chen P (2011). Isolation and characterization of cellulose nanofibers from four plant cellulose fibers using a chemical-ultrasonic process. *Cellulose* 10:433-442.
- Cordeiro N, Gouveia C, Jacob JM (2011a). Investigation of surface properties of physico-chemically modified natural fibers using inverse gas chromatography. *Ind. Crop Prod.* 33:108-115.
- Cordeiro N, Gouveia C, Moraes AGO, Amico SC (2011b). Natural fibers characterization by inverse gas chromatography. *Carbohydr. Polym.* 84:110-117.
- 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.
- Fileto-Perez HA, Rutiaga-Quinones JG, Gonzalez-Aguila CN, Paez JB, Lopez J, Rutiaga-Quinones OM (2013). Evaluation of *Eichhornia crassipes* as an alternative raw material for reducing sugars production. *Bioresources* 8:5340-5348.
- Girisuta B, Danon B, Manurung R, Janssen L, Heeres H (2008). Experimental and kinetic modeling studies on the acid-catalysed hydrolysis of the water hyacinth plant to levulinic acid. *Bioresour. Technol.* 99:8367-8375.
- Gouveia FL, Oliveira RMB, Oliveira TB, Silva IM, Nanscimento SC, Sena KXFR, Albuquerque JFC (2009). Synthesis, antimicrobial and Cytotoxic activities of some 5- arylidene-4-thioxo-thiazohdine-2-ones. *Eur. J. Med. Chem.* 44:2038-2043.
- Gupta VK, Carrott PJM, Ribeiron MMLR, Suhas (2009) Low-cost adsorbents: Growing approach to Wastewater Treatment-A review. *Critic. Rev. Environ. Sci. Technol.* 39:783-842.
- Hubbe MA, Park J, Park S (2014). Cellulosic substrates for removal of pollutants from aqueous systems. A review. Part4. Dissolved petrochemical compounds. *Bioresources* 9:7782-7925.
- Irfan M, Syed Q, Abbas S, Sher MG, Baig S, Nadeem M (2011). FTIR and SEM analysis of thermo-chemical fractionated sugarcane bagasse. *Turk. J. Biochem.* 36:322-328.
- Kaur S, Rani S, Mahajan S, Kumar R (2013). Adsorption kinetics for removal of hazardous dye Congo red by biowaste materials as adsorbents. *J. Chem.* Volume 2013, Article ID 628582, 12 pages.
- 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.* 223:2943-2953.
- Kubo S, Kadla JF (2008). Thermal decomposition study of isolated lignin using temperature modulated TGA. *J. Wood Chem. Technol.* 28:106-121.
- Lim SF, Zheng YM, Zou SW, Chen JP (2008). Characterization of copper adsorption onto an alginate encapsulated magnetic sorbent by a combined FT-IR, XPS and mathematical modeling study. *Environ. Sci. Technol.* 42:2551-2556.
- Liu CC, Wang MK, Chiou CS, Li YS, Lin YA, Huang SS (2006). Chromium removal and sorption mechanism from aqueous solutions by wine processing waste sludge. *Ind. Eng. Chem. Res.* 45:889-8899.
- Low KS, Lee CK, Tan KK (1995). Biosorption of basic dyes by water hyacinth roots. *Bioresource Technology* 52(1): 79-83. DOI: 10.1016/0960-8524(95)00007-2.
- Mahamadi C (2011). Water hyacinth as a biosorbent: A review. *Afr. J. Environ. Sci. Technol.* 5(13):1137-1145.
- Mahamadi C, Mawere E (2013). Kinetic modelling of methylene blue and crystal violet dyes adsorption on alginate-fixed water hyacinth in single and binary systems. *Am. J. Anal. Chem.* 4:17-24.
- Martone PT, Estevez JM, Lu F, Ruel K, Denny MW, Somerville C, Ralph J (2009). Discovery of lignin in seaweed reveals convergent evolution of cell-wall architecture. *Curr. Biol.* 19:169-175.
- Miretzky P, Cirelli AF (2010). Cr (VI) and Cr (III) removal from aqueous solution by raw and modified lignocellulosic materials: A review. *J. Hazard. Mater.* 180:1-19.
- Modenes AN, Ross AA, Souza BV, Dotto J, Geraldi CQ, Espinoza-Quinones FR, Kroumov AD (2013). Biosorption of BF-4B reactive red dye by using leaves of macrophytes *Eichhornia crassipes*. *Int. J. Bioautomation* 17(1):33-44.
- Mukaratirwa-Muchanyereyi N, Kugara J, Zaranyika MF (2015a). 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.* 9:282-291.
- Mukherjee R, Nandi B (2004). Improvement of *in vitro* digestibility through biological treatment of water hyacinth biomass by two Pleurotus species. *Int. Biodeterior. Biodegradation* 53:7-12.
- Muramoto S, Oki Y, Nishizaki H, Aoyama I (1989). Variation in some element contents of water hyacinth due to cadmium or nickel treatment with or without surface active agents. *J. Environ. Sci. Health A24*:925-934.
- Nath A, Sudip C, Chiranj B (2014). Bioadsorption of industrial dyes from aqueous solution onto water hyacinth (*Eichhornia crassipes*): Equilibrium, kinetic and sorption mechanism study. *Desalination Water Treat.* 52(7-9):1484-1494.
- Nigam A (2002). Bioconversion of water hyacinth (*Eichhornia crassipes*) hemicelluloses acid hydrosylate to motor fuel ethanol by xylose-fermenting yeast. *J. Biotechnol.* 97:107-116.
- Parikh VM (1974). Absorption spectroscopy of organic molecules, Addison-Wesley, Reading, Massachusetts.
- Poddar K, Mandal L, Banerjee GC (1991). Studies on water hyacinth (*Eichhornia crassipes*) - Chemical composition of the plant and water from different habitats. *Indian Vet. J.* 68:833-837.
- Priya ES, Selvan PS (2014). Water hyacinth (*Eichhornia crassipes*) – An efficient and economic adsorbent for textile effluent treatment – A review. *Arabian J. Chem.* in Press.
- Rajamohan N (2009). Equilibrium studies on sorption of an anionic dye onto acid activated water hyacinth roots. *Afr. J. Environ. Sci. Technol.* 3:399-404.
- Rajamohan N, Rajasimman M, Rajeshkannan R, Sivaprakash B (2013). Kinetic modeling and isotherm studies on a batch removal of acid red 114 by an activated plant biomass. *J. Eng. Sci. Technol.* 8(6):778-792.
- Rezania S, Ponraj M, Din MFM, Songip AR, Sairan FM, Chelliapan S (2015). The diverse applications of water hyacinth with main focus on sustainable energy and production for new era: An overview. *Renew. Sustain. Energy Rev.* 41:943-954.
- Saltabas O, Tekar M, Konuk Z (2012). Biosorption of cationic dyes from aqueous solution by water hyacinth roots. *Glob. Nest. J.* 14(1):24-31.
- Southichak B, Nakano K, Nomura M, Chiba N, Nishimura O (2006). *Phragmites australis*: A novel biosorbent for the removal of heavy metals from aqueous solution. *Water Res.* 40:2295-2302.
- Sundari MT, Ramesh A (2012). Isolation and characterization of cellulose nanofibers from the aquatic weed water hyacinth - *Eichhornia crassipes*. *Carbohydr. Polym.* 87(2):1701-1705.

- Tahir H, Alam U (2014). Lignocellulosic non-conventional low cost biosorbent for elution of comassie brilliant blue (R-250). *Int. J. Chem.* 6:56-72.
- Tarawou T, Horsfall Jr M, Vicente JL (2005). Adsorption of Methyl red by water hyacinth (*Eichhornia crassipes*). *Biomass. Chem. Biodivers.* 4:2236-2245.
- Thiebaud S, Borredon ME (1995). Solvent-free wood esterification with fatty acid chlorides. *Bioresour. Technol.* 52:169-173.
- Tran VS, Ngo HH, Guo W, Zhang J, Liang S, That CT, Zhang X (2015). Typical low cost biosorbents for adsorptive removal of specific organic pollutants from water. *Bioresour. Technol.* 182:353-363.
- Tserki V, Matzinos P, Kokkou S, Panayiotou C (2005). Novel biodegradable composites bases on treated lignocellulosic waste flour as filler. Part I. Surface chemical modification and characterization of waste flour. *Compos. Part A Appl. Sci. Manuf.* 36(7):965-974.
- 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.
- Tshabalala MA, Jakes J, Vanlandingham MR, Wang S, Peltonen J (2005). Surface characterization. In Rowell, R.M.(ed), *Handbook of Wood Chemistry and Wood Composite*. CRC Press, Boca Raton, pp. 217-247.
- Uddin MD, Islam MT, Chakrabarti MH, Islam MS (2013). Adsorptive removal of methylene blue from aqueous solutions by means of HCl treated water hyacinth: isotherms and performance studies. *J. Purity Utility React. Environ.* 2(3):63-84.
- Woverton BC, McKown MM (1976). Water hyacinth for removal of phenols from polluted water. *Aquat. Bot.* 2:191-201.
- Zafeiropoulos NE, Williams DR, Baillie CA, Matthews FL (2002). Engineering and characterisation of the interface in flax fibre/polypropylene composite materials. Part I: Development and investigation of surface treatments. *Compos. Part A Appl. Sci. Manuf.* 33(8):1083-1093.
- 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.* 171:780-785.