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Spectroscopic analyses of water hyacinth: FTIR and modeling approaches

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ABSTRACT

Water hyacinth has received attention because of its potential to remove pollutants when utilized as a biological filtration system. It could remove several heavy metals as well as some organics. In the present work, water hyacinths from fresh as well as polluted water were collected. FTIR and XRF were utilized to study the structure of water hyacinth collected from different media. Semiemperical quantum mechanical calculations were utilized at PM6 level of theory to simulate the molecular structure of the plant based on the obtained experimental results. Results concluded that, water hyacinth could be described as a composite of cellulose and lignin as well as some metal oxides.

Keywords: Phytoremediation, Water hyacinth, FTIR, XRF and PM6.

INTRODUCTION

Aquatic plants such as water hyacinth showed potential use in the remediation of pollutants from aquatic environment [1]. It could be utilized in aquatic macrophytes treatment system (AMATS) which is a well established environment protective technique as a phytoremediation procedure for removing pollutants [2]. Water hyacinth that belongs to the family pontederiaceae stands as a challenging, most productive invasive aquatic plant on Earth posing extreme risk to the ecosystem. Water hyacinth has originated in the American tropics and spread to all tropical climate countries. Due to vegetative reproduction and vigorous growth rate of this plant, it dramatically impacted water flow, blocked sunlight from reaching native aquatic plants, and starved the water of oxygen, often killed fish and also acted as a prime habitat for mosquitoes. A typical biomass from land plants is composed of 30–50% cellulose, 20–40% hemicellulose and 15–30% lignin. It was also found to have high nitrogen content and in combination with cow dung it can be used for biogas production [3]. It has high tolerance to pollution, and its heavy metal and nutrient absorption capacities qualify it for use in wastewater treatment ponds. The application of water hyacinth in effluent treatment is indicating the biosorption capacity of the water hyacinth for the treatment of wastewater including heavy metals as well as some industrial effluent [4-9]. However, phytoremediation is easy to operate and cost-effective and can convert wastewater nutrients to valuable biomass. Moreover, aquatic plants can directly absorb nutrients from wastewater and do not compete with crops for agricultural land [10-13]. A host of aquatic plants, such as water hyacinth, duckweed, water lettuce, pennywort, Canna Lily and reed, have been used for wastewater treatment. Plenty of previous studies have shown that in these aquatic plants, water hyacinth has the largest production rates (more than 140 t/ha/year) and the best wastewater treatment performance [14-15]. However, comprehensive comparison, including biomass production, nutrient recovery efficiency and utilization potential of biomass, was not assessed in these studies. Additionally, previous studies show that duckweed has the higher protein (more than 40%), starch content (more than 45%) and lower fiber content than the other aquatic plants, hence providing it with more utilization potential [16-17]. It is indicated that, carboxyl group plays an important role in the removal of pollutants [18]. Later on, the mechanism of pollution control using modified water hyacinth re-introduced [1] the possible interaction between the modified plant and Cd has been proven. The modified water hyacinth is utilized to a wastewater containing Cd, the results were satisfactory in time as short as 2 hours [19]. A model is prepared in order to describe the mechanism of its interaction with the surrounding inorganic structures [20]. Furthermore, the investigation was conducted for comparison between the plants physical as well as chemical treatment. It is shown that the crystallinity of the plant is partially enhanced after microwave heating; which means that physical treatment of the plant could enhance its atomic arrangements [21]. Based upon these studies water hyacinth could be described as cellulose like material [21, 22]. Recently microsphere from chitosan and dried water hyacinth was prepared. The prepared microsphere shows the potential of removing Pb from wastewater 1.62 times higher than the dried water hyacinth [23].

In the present work FTIR and XRF are conducted to analyze water hyacinth collected from different media. Based on spectroscopic data, molecular modeling at PM6 level was conducted to prepare a model to simulate the molecular structure of the plant.

MATERIAL AND METHODS

2.1 Samples collections and preparation

- Triplicates of water hyacinth were collected from four locations. River Nile at Tamooh, Giza is considered as a control.

Three drainages namely

1- Qalyob agricultural drainage.
2- Shoubra Elkhima agricultural drainage.
3- Shoubra Elkhima municipal drainage.

- Samples were washed thoroughly then divided into root and shoot.
- Samples were oven dried at 105 ºC over night to get ride out moisture. The dried plants (root and shoot) were ground separately in a bladed mixer to less than 0.2 mm.
- 2.0 mg of the dried samples were mixed with 198.0 mg KBr then pressed in pellet to be ready for FTIR analyses following disc technique.
- Part of the dry sample was mixed for three minutes with low contamination binder (Wax, $C_6H_8O_3N_2$) in a mass ratio binder: sample is 4:0.9. The wax was used due to its low absorption and low contamination for the elements of interest, and the mixing time has been chosen to prevent sample caking and increase the pellet stability. The samples were transferred to Al cups and pressed using a hydraulic press (Herzog hydraulic HTP40, UK) at a pelletizing pressure of 120 $KN.cm^{-2}$ for three minutes. High pressure and long pressing time was used for preparing pellet samples in order to confirm the stability of x-ray emission of the samples [24]. Afterwards, the pellet samples were ready for being exposed to a radiation source of the X-Ray fluorescence (XRF) technique for quantitative analysis of the samples.

2.2. Instrumentation

Fourier Transform Infrared Spectroscopy (FTIR)

Jasco FTIR 430 Fourier Transform Infrared Spectrometer was used for recording the obtained IR spectra. Spectra were recorded in a spectral range of 4000-400 cm^{-1}, resolution of 4 cm^{-1} and scan speed is 2 mm/s. Samples were introduced as KBr pellet.

- Wavelength Dispersive X-Ray Fluorescence (WDXRF)

A multichannel high performance sequential Wavelength Dispersive X-Ray Fluorescence (WDXRF) spectrometer (Axios 2005, PANalytical Netherlands) was used for quantitative analysis of water hyacinth samples. The WDXRF allowed rapid and accurate elemental analysis and was able to deal with the different types of samples in the form of solids, fused beads, pressed or loose powder and liquid samples.

The X-ray tube in the present WDXRF spectrometer had Rh anode and was operated at a maximum power of 4 kW and a maximum current of 160 mA. To obtain high resolution spectra, five dispersive crystals were used with the WDXRF, namely LiF200, PE curved, PXI, LiF220 and Ge curved. To recognize all the elements in the studied samples, the characteristic radiation of the major, minor and trace elements were recorded under vacuum in ten different scans. Each scan covers a certain number of the expected elements and the peak areas of the characteristic radiation were measured. Gas proportional, Duplex and scintillation counters were used for recording the intensities of the characteristic radiations.

2.3. Calculation Details

Molecular modeling calculations were performed on personal computer using SCIGRESS program system at Spectroscopy Department, National Research Centre [25]. Geometries of the studied structures were optimized at Semiemperical PM6 [26] method and vibrational spectra were calculated at the same level of theory. Some physical parameters such as heat of formation, total energy, total dipole moment, ionization potential and molecular dimension were calculated at PM6 semiemperical quantum mechanical method.

RESULTS AND DISCUSSION

3.1. FTIR and WXRF Results

FTIR was utilized to study samples collected from different media. Fig. (1) and Fig. (2) present the FTIR absorption spectra of water hyacinth root and shoot collected from the Nile as well as three drainages. The assignment of water hyacinth was already discussed in our previous work [1, 23]. Table 1 presents the assignment for root and shoot. It is clear from Fig. (1) and Fig. (2) that the molecular structure for water hyacinth is the same for the four collected samples. The spectra show the characteristics bands for polysaccharides such as cellulose and proteins. These findings are in good agreement with those obtained before: that water hyacinth contains carbon, crude protein, amino acids, phosphorus, cellulose, lignin and flavonoids [27].

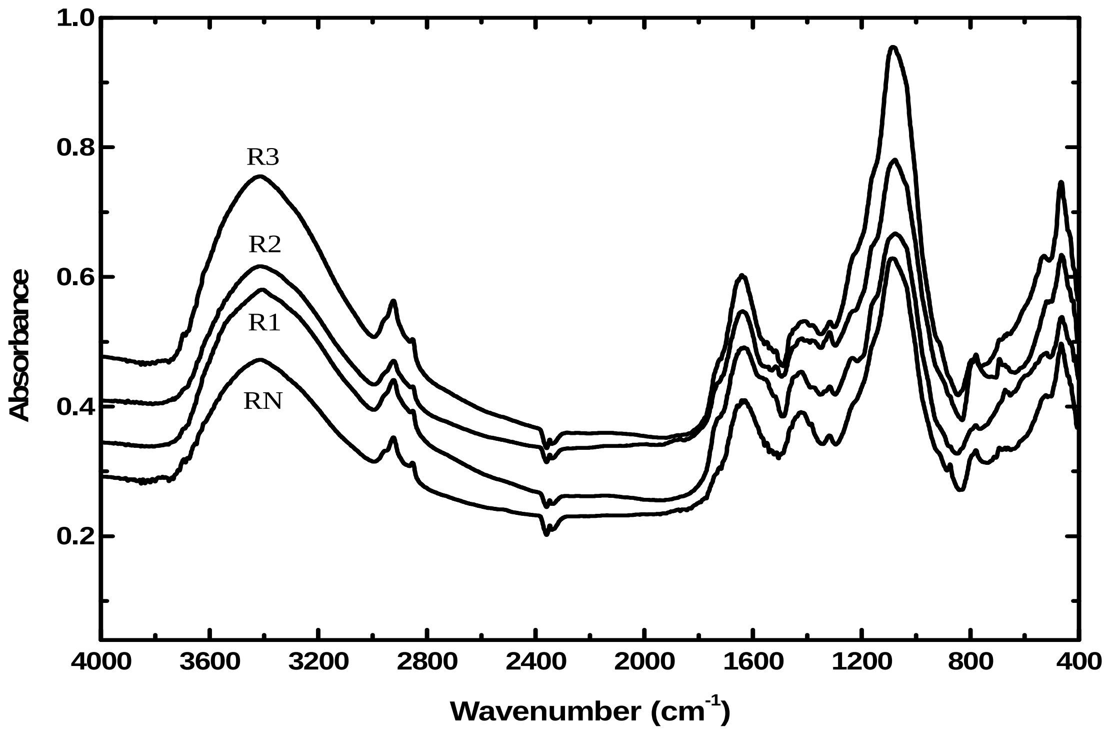

Fig. (1) FTIR absorbance spectra for water hyacinth root which collected from different media

It is important to describe the elemental composition of the plant using XRF technique. As shown in Table 2 the results of metals as well as metal oxides are obtained with the help of WXRF. Results indicate in general the increase in metals as well as metal oxides contents in root more than in shoot. Control samples show lower values as compared with other samples. Contamination increases the level of metals such as Zn, Ba, Sr, Cu and Zn. The level of metal oxides varies depending on the source of contamination and different locations from which water hyacinth samples were collected from the river Nile. As a general conclusion from these XRF data one can notice that the plant contains metal oxides similar to the structure of montmorillonite, so that the plant contains clay minerals like structure.

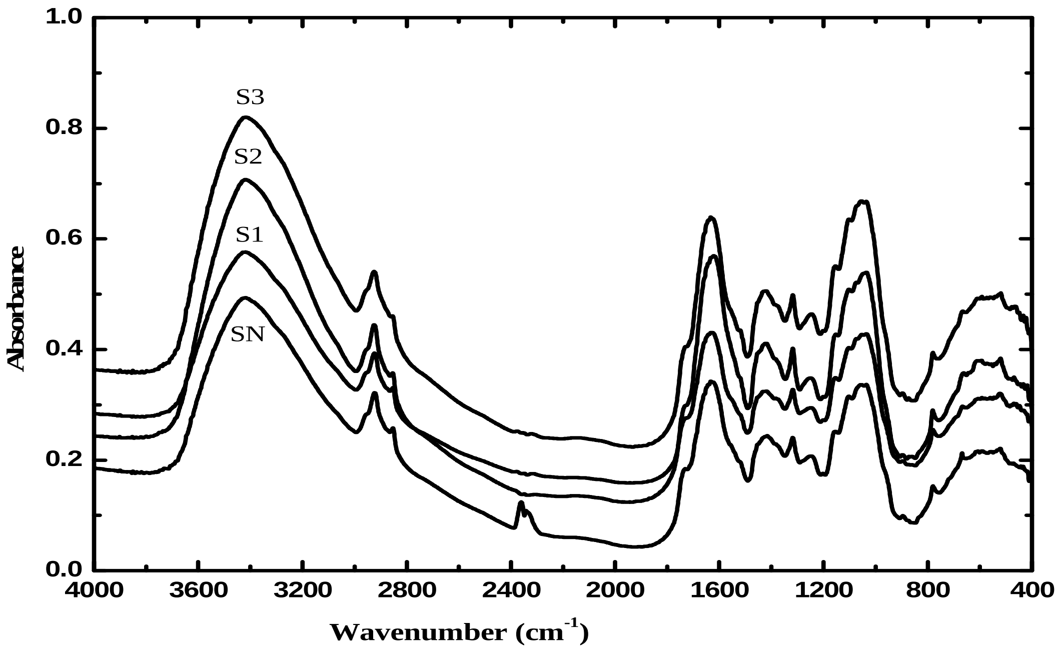

Fig. (2) FTIR absorbance spectra for water hyacinth shoot which collected from different media

Table 1. The band assignments of water hyacinth plant root and shoot

Shoot	Root	Band Assignment
3400– 3366	3388	OH
2925 – 2854	2922 – 2852	CH
1732.7	1738.5	C=O
1645.9	1634.4	C=O
1624.7		C-O symm.,
1590.0		C-O asymm.,
	1516.7	C-O of CHO
1421.3	1422.2	C-O of cellulose
1384.6	1384.6	OH phenolic
1318.1	1371.1	CH
1035.6	1035.6	OH

Combining both results one can conclude that water hyacinth is a composite of cellulose/lignin/protein/metal oxides. Those could be representing the functional groups obtained by FTIR and the elemental analyses obtained by XRF. These data could furnish the basis for molecular modeling in order to simulate the structure of the plant as in the following section.

Table 2. The XRF concentrations of metals oxides as percentage; metal as ppm for water hyacinth plant root and shoot

	RC	R1	R2	R3	SC	S1	S2	S3
SiO_2	3.30	11.95	3.31	4.92	0.30	0.33	0.30	0.13
Fe_2O_3	0.86	6.02	2.45	3.98	0.36	0.21	0.19	0.07
K_2O	1.31	4.02	2.40	2.40	2.28	5.30	3.81	4.01
Al_2O_3	2.72	3.92	1.20	1.58	0.50	0.11	0.09	0.03
CaO	1.89	3.32	4.73	2.73	2.24	2.65	2.94	2.20
P_2O5	0.24	1.20	2.05	2.40	0.16	0.68	0.83	0.50
MgO	1.43	1.20	0.78	0.46	1.18	0.42	0.54	0.23
Na_2O	--	1.14	1.40	0.67	--	0.12	0.70	1.38
SO_3	0.65	0.99	2.05	2.71	0.46	0.18	0.34	0.49
MnO	0.16	0.71	1.11	0.48	0.03	0.05	0.16	0.03
TiO_2	0.13	0.66	0.23	0.29	0.01	0.04	0.03	--
Zn	380	478	128	325	75	53	46	41
Ba	194	239	278	245	84	--	--	--
Sr	112	262	344	194	118	116	181	95
Cu	36	185	162	159	20	116	215	--
Zr	33	120	65	58	10	16	34	15

3.2. Molecular Modeling Simulation for Water Hyacinth

Based on the previous results, water hyacinth is composed of cellulose; lignin and some metal oxides. Of course the plant contains protein but for dried plant at 105°C over night the protein has suffered from degradation. Accordingly the plant in its dry form is tested as a composite of 3 units of cellulose; one unit of lignin; metal oxides like CaO; FeO and $Al(OH)_3$ that interacted with this composite through the O-Linkage connecting the cellulose and lignin.

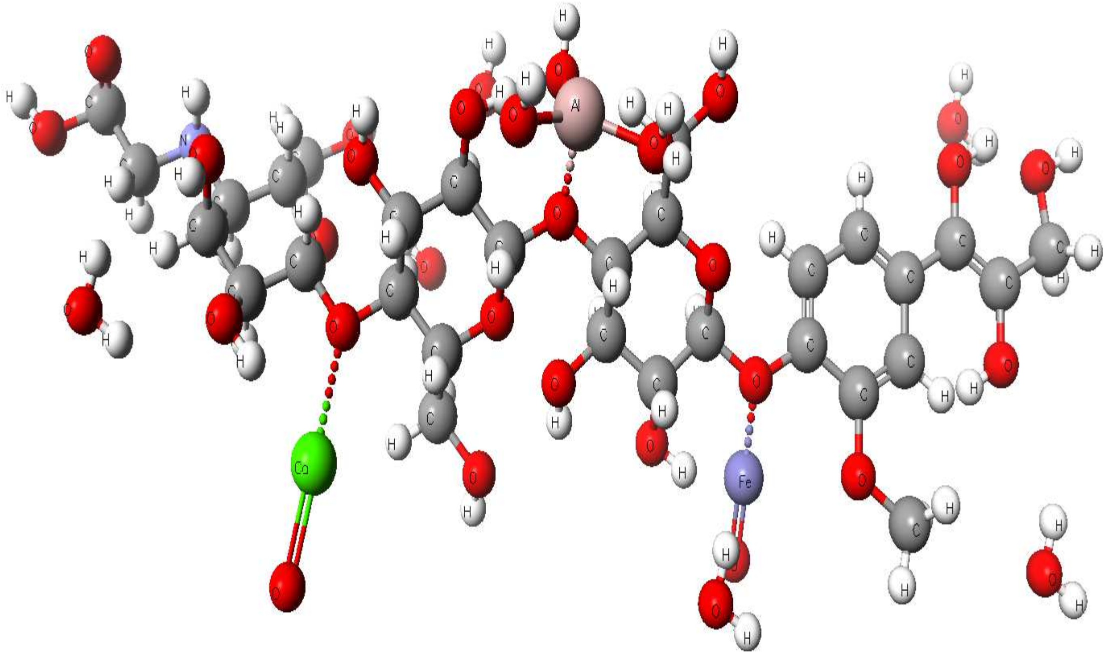

Fig. (3) Simulated water hyacinth structure calculated at PM6 semiemperical quantum mechanical method. The structure consists of three cellulose units, one lignin unit, amino acid (glycine), CaO, FeO, $Al(OH)_3$ and five water molecules

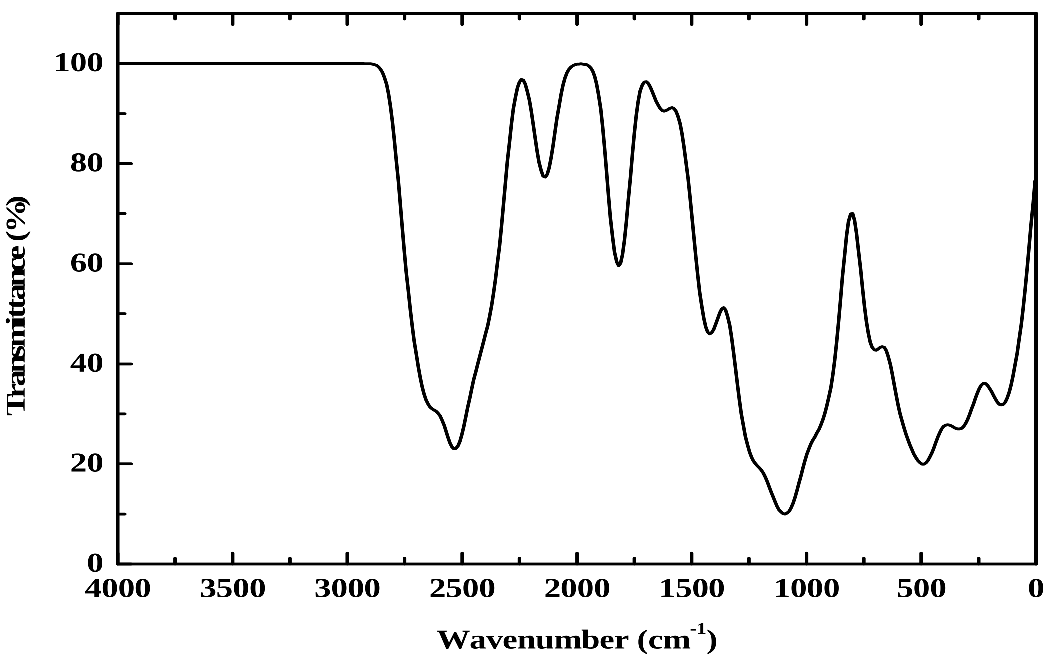

Fig. (4) Calculated vibrational spectrum for water hyacinth structure calculated at PM6 semiemperical quantum mechanical method. The structure consist of three cellulose units, one lignin unit, amino acid (glycine), CaO, FeO, $Al(OH)_3$ and five water molecules

Fig. (3) presents the simulated water hyacinth structure which was calculated at PM6 semiemperical quantum mechanical method. The structure consists of three cellulose units, one lignin unit, amino acid (glycine), CaO, FeO, $Al(OH)_3$ and five water molecules. Semiempirical calculations indicate that this assumption could be a real one. Furthermore, the results indicate that the structure corresponds to the optimized structure at PM6 level of theory.

Fig. (4) presents the calculated vibrational spectrum of this model. Assignment of the vibrational characteristics at this level of theory is out of scope while the calculated vibrational spectra are only an indication for the occurrence of optimization of the studied structure.

Table 3 presents some physical parameters for the water hyacinth model. The calculated heat of formation is -1596.640 Kcal/ mol while the total energy is -14508.859 eV. The calculated total dipole moment is 9.213 Debye, the ionization potential is 9.089 eV and molecular dimension for the model is 20.733 Ǻ. It has been indicated earlier that higher values of dipole moment are an indication for the reactivity of the given structure [28-29]. Within the frame of quantum mechanical data, water hyacinth possesses high values of total dipole moment indicating its ability to interact with the surrounding media.

Table 3. Calculated heat of formation (HF) as Kcal/mol, total energy (TE) as eV total dipole moment (TDM) as Debye, ionization potential (IP) as eV and molecular dimension (MD) as Ǻ, for simulated water hyacinth structure calculated at PM6 semiemperical quantum mechanical method.

	HF	TE	TDM	IP	MD
Cel3-Lig1-Gly-5W-MO	-1596.640	-14508.859	9.213	9.089	20.733

CONCLUSION

Water hyacinth from different media was subjected to XRF and FTIR spectroscopic analyses. Based upon experimental data the plant is simulated with PM6 level of theory. The model simulates water hyacinth as a composite of cellulose, lignin, amino acids, metal oxides such as FeO and CaO, and metal hydroxide such as Al $(OH)_3$. The whole composite is hydrated with five water molecules. The present work will be extended in order to simulate the plant with higher level of theory.

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REFERENCES

[1] M Ibrahim; T. Scheytt Increasing the ability of Water hyacinth for removing Cadmium. Second International Congress on Environmental Planning and Management, 5-10 Aug., **2007** TU-Berlin, Berlin, Germany.
[2] W Zhang; S Chen; S. Yu; Y Yin. *J. Cryst. Growth* **2007**, 308, 122.
[3] UN Rai; RD Tripathi; P Vajpayee; V Jha; MB Ali. *Chemosphere*, **2002**, 46, 267.
[4] A Bhattacharya; P Kumar. *P.EJEAFChe*, **2010**, 9, 112.
[5] HN Chanakya. S Borgaonkar; G Meena; KS Jagadish. *Bioresour. Technol.*, **1993**, 46, 227.
[6] V Singhal; JPN Rai. *Bioresour. Technol.*, **2003**, 86, 221.
[7] NW Ingole; AG J Bhole. *Water SRT-Aqua*, **2003**, 52 119.
[8] S Liao; WJ Chang. *Aqua. Plant Manage*, **2004**, 42, 60.
[9] MW Jayaweera; JC Kasturiarachchi. *Water Sci. Technol*., **2004**, 50, 217.
[10] Z Yonggui; F Yang; J Yanling; H Jun; B Shu, B.Tian, F. Zhiming, H.Feng, W.Hai, Z. *Bioresource Technology*, **2014**, 163, 82.
[11] M Kandawire; EG Dudel. *Biorem. Biodiv. Bioavail*., **2007**, 1, 56.
[12] NK Shammas; LK Wang. *Environ. Biotechnol*., **2010**, 10, 567.
[13] J Cheng; AM Stomp. *Clean Soil Air Water*, **2009**, 37, 17.
[14] A. Abdelhamid, A Gabr. *Arch. Anim. Nutr*., **1991**, 41, 745.
[15] TA DeBusk; JE Peterson. KR Reddy. *Ecol. Eng*., **1995**, 5, 371.
[16] KR Reddy; WF Debusk. *Econ. Bot.*, **1985**, 39, 200.
[17] Q Chen; Y Jin; G Zhang Y Fang; Y Xiao; H Zhao. *Energies*, **2012**, 5, 3019.
[18] H Zhao; K Appenroth; L Landesman; AA Salmeán; E Lam. *Plant Mol. Biol*., **2012**, 78, 627.
[19] M Ibrahim; AA Shaltout; M Soylak; AF Jalbout; DE Kamal. *J. Iran. Chem. Soc.*, **2009**, 9, 364.
[20] M Ibrahim; O Kühn; T Scheytt. *Open Chem.Phys.J.*, **2009**, 2, 1.
[21] M Ibrahim; R Mahani; O Osman; T Scheytt. *Open Spectrosc.J.*, **2010**, 4, 32.
[22] M Ibrahim; Z Al-Fifi. *Open Spectrosc.J*., **2010**, 4, 10.

[23] NS Ammar; H Elhaes; HS Ibrahim; W El-hotaby; MA Ibrahim. *Spectrochim. Acta A.*, **2014**, 121C, 216.
[24] RE Van Grieken; AA Markowicz. Handbook of X-Ray Spectrometry, 2nd Edition Marcel Dekker, Inc., New York, **2002**.
[25] JJP Stewart. MO-G Version 1.1A, Fujitsu Limited, Tokyo, Japan **2008**.
[26] JJP Stewart. *J. Mol. Mod*. 13 (**2007**) 1173.
[27] HT Tham, Water Hyacinth (Eichhornia crassipes)- Biomass Production, Ensilability and Feeding Value to Growing Cattle, Doctoral Thesis Swedish University of Agricultural Sciences Uppsala **2012**.
[28] M Ibrahim; H El-Haes. *Int. J. Environ. Pollut*., **2005**, 23, 417.
[29] M Ibrahim; A-A Mahmoud. *J. Comput. Theor. Nanosci*., **2009**, 6, 1523.