

Molecular Spectroscopic Study of Water Hyacinth Collected from Different Media

¹Osama Osman, ¹Fatma Atia, ¹Nagwa Abdel Hakeem, ²Mohamed Mansour Al Neklawy and
²Amin Fahem

¹Spectroscopy Department, National Research Centre, 12311 Dokki, Cairo, Egypt

²Physics Department, Faculty of Science, Helwan University, Cairo, Egypt.

Abstract: This study was conducted to evaluate the elemental as well as molecular structure of water hyacinth. Samples were collected from three drainage of wastewater, municipal and agricultural pollution. X-Ray Fluorescence spectroscopy (XRF) results show that the concentration of metals and metal oxides are higher in plant root than in plant shoot. The highest concentration of Pb has been detected in the root which collected from the municipal wastewater drainage while the plant root of the agriculture wastewater has the highest concentration of metal oxides. Fourier Transformation Infrared Spectroscopy (FTIR) was used to study the molecular structure of the plant. Results suggested a role for metal oxides in controlling organic acids in plants. Furthermore, the plant could uptake metals from water which transfer carboxyl group around 1740 cm^{-1} into metal carboxylate around 1640 cm^{-1} .

Key words: FTIR, XRF, heavy metals, organic pollution and Water hyacinth.

INTRODUCTION

Fourier transform infrared spectroscopy (FTIR) is a powerful technique for studying molecular structures. Accordingly many researchers apply FTIR in their studies. In environmental studies Ibrahim, M. and Abd-El-Aal, M. (2008); Ibrahim *et al.* (2008), Ibrahim *et al.* (2009). Biological studies Ibrahim *et al.* (2010), Ibrahim, M. (2010). Biopolymers; such as cellulose Ibrahim, M. and Osman, O. (2009); chitosan Ibrahim, M. *et al.* (2009); aquatic plants Ibrahim, M. and AlFifi, Z (2010), Ibrahim, M. *et al.* (2010). FTIR and molecular modeling proves that functional group like COOH could enhance the ability of the dry plant for mediating heavy metals Ibrahim, M. and Scheytt, T. (2007); Ibrahim, *et al.* (2009). Furthermore, the plant could be used to mediate both organic as well as inorganic pollution Ibrahim *et al.* (2009). Water hyacinth, *Eichhornia crassipes* (Mart. Solms) is a tropical aquatic plant belonging to the pickerelweed family (*Pontederiaceae*). The plants grow abundantly in wide regions of the world Center, T. (1994). It appeared in Egypt for the first time early in the 1890s Gopal, B. (1987). It is listed as one of the most productive plants on earth. It can double its size in 5 day Malik, A. (2007). The phenomena of phytoremediation by water hyacinth was demonstrated in constructed wetlands in Taiwan Liao, S. and Chang, W. (2004). High absorption capacity for Pb, Cu, Zn was recorded. A significant metal removal (over 90%) from aluminum industry effluents has also been obtained by employing water hyacinth Roldin, G. (2002). Later on the water hyacinth can be utilized to accelerate the removal and degradation of agro-industrial wastewater polluted with ethion Xia, H. (2006). Nitric- acid treated water hyacinth can be used as an adsorbent for the removal of methylene blue dye from aqueous solutions El-Khairi, M. (2008). It was investigated that non living water hyacinth roots have the ability of sorption of Uranium from aqueous solutions Shawky, *et al.* (2005). It had been shown that more than 93% of arsenite (As(III)) and 95% of arsenate (As(v)) were removed from a solution containing $200\mu\text{g As/L}$ within 60min of exposure to a powder produced from dried roots Al-Ramalli, S., *et al.* (2005). It was demonstrated that the water hyacinth displays effective antioxidative activity like soya and garlic Bodo, R. *et al.* (2004).

Although XRF and FTIR were conducted previously on water hyacinth collected from the Nile, it is necessary to study water hyacinth in different waste waters. Accordingly, XRF will be used to evaluate the level of metals and metal oxides in plant parts. Also FTIR spectroscopy techniques will be used to study the molecular structure of the plant which collected from different media.

MATERIALS AND METHODS

Sample preparation and collection:

Corresponding Author: Osama Osman, Spectroscopy Department, National Research Centre, 12311 Dokki, Cairo, Egypt
Email: osamaosman69@yahoo.com

Water hyacinth was collected from three drainage of wastewater, municipal and agriculture pollution. The plant was washed carefully with tap water to get rid of any contamination, then it was divided into two parts namely root and shoot. Both of root and shoot was dried at 105 °C for 24 h. The dried plant was cut into small pieces and then ground in a hardened steel vial containing two hardened steel balls. The vial was fitted to aspex-mixer mill which was rotated several times for short periods. The obtained powder was then sieved to different particle sizes to be ready for the different measurement.

R1 root, S1 shoot of sample which is collected from agriculture wastewater drainage. R2 root, S2 Shoot of sample which is collected from agriculture wastewater drainage polluted with municipal wastewater, R3 root, and S3 shoot of sample which is collected from municipal wastewater.

Instrumentation:

For FTIR measurement:

The FTIR spectra was collected for the studied samples at the spectroscopy department, National Research Center, Egypt using the spectrometer JASCO, FTIR-300 E, Japan, which cover the range from 400 to 4000 cm⁻¹. The KBr disc technique was followed for the FTIR study, that is the obtained powder was then sieved to particle size fractions ranging from 180 to 125 μm in diameter. A weight of 2 mg of these powders was thoroughly mixed with 198 mg of specpure KBr to give 1% concentration. The mixing was carried out for suitable time in an agitate mortar. The mixtures were then pressed in a special die under vacuum hydraulic press (at 6 tons) to form transparent discs.

For X-Ray Fluorescence (XRF):

AXIOS, WD-XRF Sequential Spectrometer (PANalytical,2005) was used for XRF analysis. Each sample was grinded in Herzog mill to rich fine powder then 7 g., of the fine powder of each sample was mixed with 1.6 g., of binding wax in small mill, on speed 380 cr/mnt, for one minute. Then it was put in aluminium cup, after that it pressed in automatic pressed machine.

RESULTS AND DISCUSSION

Role of Metal Oxides:

Metal oxides play an important role in controlling organo-metalic interaction in the environment. Vermoehlen *et al.* (2000) present feasibility of numerous possible structures for the interaction of organic structures and metal oxide surfaces. They indicate as seen in figure 1 the adsorption of organic acid onto aluminum hydroxide surface. Aaluminium hydroxides have large surfaces, and the charge of theses surfaces can change. As far as aluminium oxide is hydrated the hydroxide is formed which acts as nano metal substrate as an active surface for organic acids. In other word it is stated that hydrated aluminium hydroxides offer a wide surface for the organic acid to be adsorbed onto Vermoehlen *et al.* (2000). It is concluded upon DRIFT-FTIR and Ab Initio calculations that the carboxylate oxygen's of the organic acid bridge an Al³⁺-octahedral dimer in a ligand-exchange inner-sphere complex as indicated in the model in figure 1. This finding is confirmed later by Ibrahim, M. *et al.* (2008). Accordingly the level of metal oxides is studied by means of X-Ray Fluorescence Spectroscopy (XRF) in order to estimate their levels in water hyacinth.

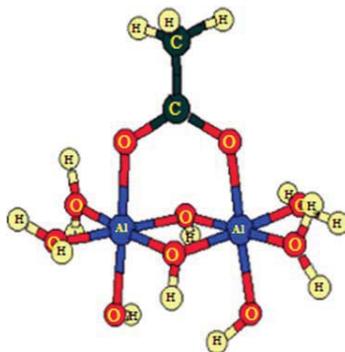


Fig. 1: Model structures representing Vermoehlen model for $[Al_2(OH)_4(H_2O)_4(CH_3COO)]$ which indicates the adsorption of organic acid onto hydrated aluminium hydroxide, Red Balls: Oxygen, Yellow: Hydrogen Black: Carbon and Blue: Aluminium.

Levels of Metals and Metal Oxides in Water Hyacinth Root and Shoot:

In the present study, XRF was utilized to determine the concentration of metal and metal oxides in both root and shoot of the plants collected from different drainages.

As seen in the table 1 the concentration of metal oxides showed higher concentration in root samples as compared with shoots samples. The only exception is that the concentration of K_2O in shoot samples is higher than root samples. The concentration of metal oxides could be arranged according to the following decreasing order:



As a general description, the lowest values were noticed in the root and shoot of sample 3 with the exception that R3 shows higher SO_3 and P_2O_5 while S3 shows higher SO_3 and Na_2O respectively.

Table 1: Concentration of metal oxides that analyzed with XRF technique.

Constituents (Wt %)	R1	S1	R2	S2	R3	S3
SiO_2	11.95	0.33	3.31	0.3	4.29	0.13
K_2O	4.02	5.3	2.4	3.81	2.4	4.01
CaO	3.32	2.65	4.73	2.94	2.73	2.2
Al_2O_3	3.92	0.11	1.2	0.09	1.58	0.03
$Fe_2O_3^{tot.}$	6.02	0.21	2.45	0.19	3.98	0.07
MgO	1.2	0.42	0.78	0.54	0.46	0.23
Na_2O	1.14	0.12	1.4	0.7	0.67	1.38
MnO	0.71	0.05	1.11	0.16	0.48	0.03
P_2O_5	1.2	0.68	2.05	0.83	2.4	0.5
SO_3	0.99	0.18	2.05	0.34	2.71	0.49
TiO_2	0.66	0.04	0.23	0.03	0.29	

ND: Not detected

The XRF data of the studied metals is tabulated in table 2; the concentration of metals showed higher levels in root samples as compared with shoot samples. The metals of the highest concentration are Sr, Zn and Cu respectively. R3 has the lowest concentration of metals except for Pb where it found in higher levels corresponding to R3. The XRF results indicate the existence of metal oxides with high possible for hydration as a result these metals could act like aluminum and accordingly could enhances the uptake of organic acids from the aquatic environment.

Table 2: Concentration of metals that analyzed with XRF technique.

Metal (ppm)	R1	S1	R2	S2	R3	S3
As	40	ND	ND	ND	44	ND
Ba	239	ND	278	ND	245	ND
Cr	98	ND	ND	ND	ND	ND
Cu	185	116	162	215	159	ND
Ni	92	ND	58	38	ND	ND
Pb	49	ND	ND	ND	977	ND
Rb	51	ND	ND	ND	ND	ND
Sr	262	116	344	181	194	95
Zn	478	53	128	46	325	41
Zr	120	16	65	34	58	15

ND: Not detected

FTIR of water hyacinth:

The FTIR spectrum of water hyacinth root and is indicated in figures 2 –a and b. The bands assignment is tabulated in table 3. The OH band of water appears at $3380-3388\text{ cm}^{-1}$ corresponding to plant shoot and at $3419-3430\text{ cm}^{-1}$ corresponding to root samples. For plant shoot the CH stretching is located at $2913-2929\text{ cm}^{-1}$, while the same band for root is located at $2913-2929\text{ cm}^{-1}$. C=O stretching of organic acid is located at $1737-1743\text{ cm}^{-1}$ for both shoot and root. This band is not clear in the spectra at figures 2. To indicate such band deconvolution process took place in the spectral range of $1000-2000\text{ cm}^{-1}$. The deconvolution is plotted in figure 3. As far as water hyacinth is subjected to heavy metals for long times this band of C=O is shifted to $1639-1644\text{ cm}^{-1}$ and $1540-1554\text{ cm}^{-1}$ respectively. This bands are known as metal carboxylates, the shift depends on the type of metal. It is stated that each metal in hydrated form could interact with organic acid through hydrogen bonding and hence C=O is transformed into metal carboxylate Ibrahim, M. and Abd-El-Aal, M. (2008). This interaction leads to a decrease in the intensity of the C=O bands as seen in figure and increase in metal carboxylate bands as seen in figure 2. The first one ($1639-1644\text{ cm}^{-1}$) stated for the interaction

between organic acid and heavy metals while other bands (1540-1554 cm^{-1}) for the interaction between alkali metals and organic acids.

CH bending vibrations are located at 1415-1428 cm^{-1} for plant shoot and root respectively. This band followed by another one at 1313 cm^{-1} appears only in case of plant shoot. Finally the characteristic band of cellulose C-O backbone at 1027-1047 cm^{-1} for plant shoot and root.

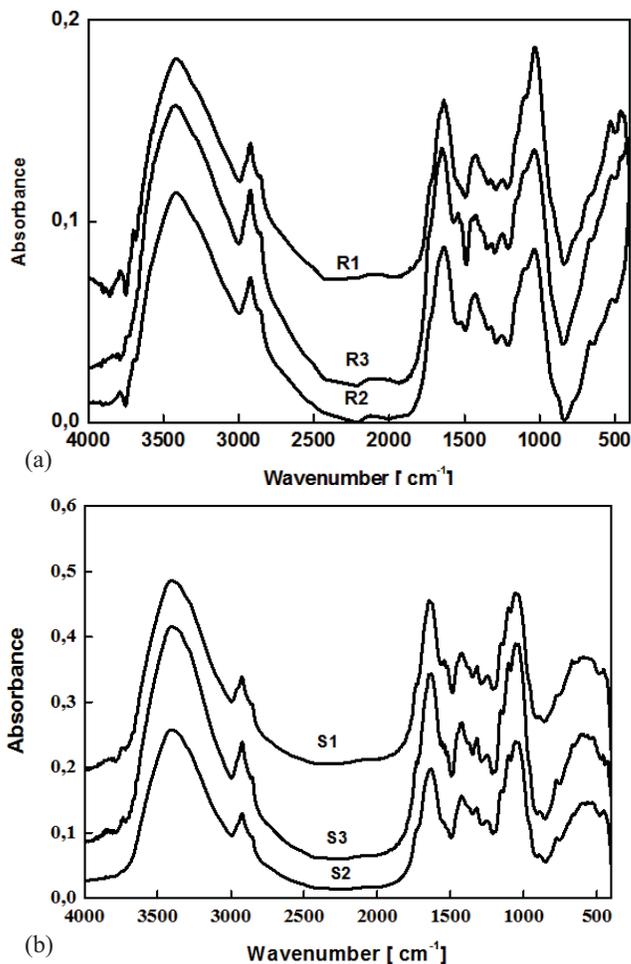


Fig. 2: FTIR absorption spectra of water hyacinth whereas (a) represents root samples and (b) represents shoot samples. R1 and S1 are samples collected from agriculture wastewater drainage. R2 and S2 are samples collected from agriculture wastewater drainage polluted with municipal wastewater. Finally R3 and S3 are samples collected from municipal wastewater.

Table 3: FTIR band assignment as cm^{-1} for the studied water hyacinth Shoot and Root.

Band Frequencies		Band assignment
Shoot	Root	
3380-3388	3419-3430	OH stretching
2913-2929	2913-2929	CH stretching
1737-1743	1737-1743	C=O
1639-1644	1639-1644	Metal carboxylate*
1536- 1540	1540-1554	Metal carboxylate**
1415-1428	1415-1428	CH bending
1313	-	CH bending
1027-1047	1027-1047	C-O backbone

*COO asymmetric stretching of heavy metals carboxylate Ibrahim, M. and M. Abd-El-Aal, (2008)

**COO asymmetric stretching of alkali metals carboxylate Ibrahim, M. and M. Abd-El-Aal, (2008)

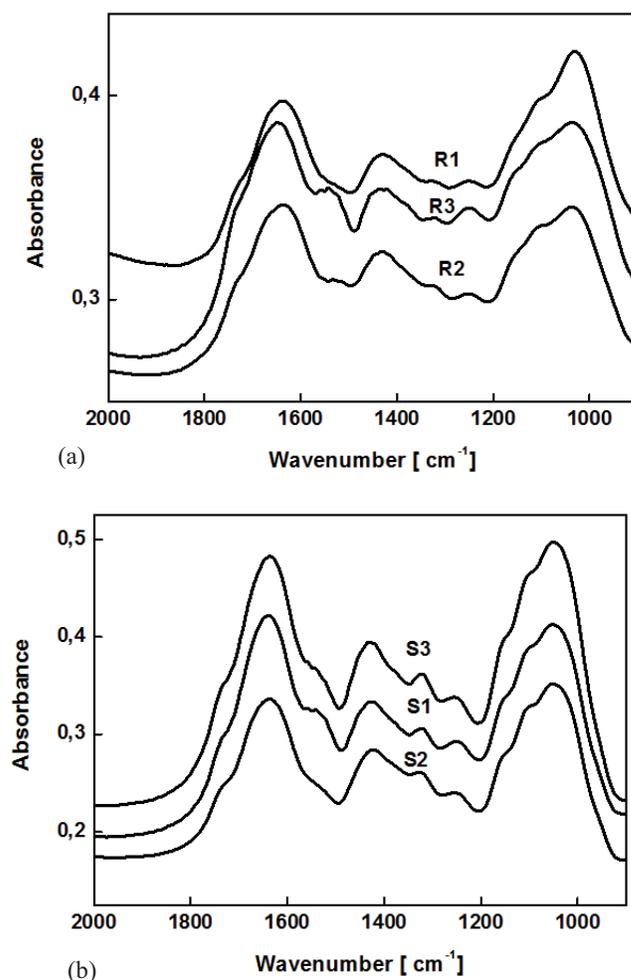


Fig. 3: FTIR Deconvolution absorption spectra of water hyacinth in the 1000–2000 cm⁻¹ whereas (a) represents root samples and (b) represents shoot samples. R1 and S1 are samples collected from agriculture wastewater drainage. R2 and S2 are samples collected from agriculture wastewater drainage polluted with municipal wastewater. Finally R3 and S3 are samples collected from municipal wastewater.

Conclusion:

The present study indicates that the media affect the structure and metal content of the plant. The present plants which collected from organic, municipal waste waters were completely different from those collected from the Nile. The concentration of metals and metal oxides are higher in plant root than in plant shoot as shown from XRF results. The existence of metal oxides in their hydrated form offers a good surface for organic acids to be adsorbed. Furthermore metals could interact with carboxyl of the plant to form metal carboxylate around 1640 cm⁻¹ this makes the band of carboxyle weak will those of metalcarboxylates are strong. From these data water hyacinth in open aquatic environment like agricultural and municipal drainage could be useful for removing both organic and inorganic pollutants.

REFERENCES

Al Ramalli, S.W., C.F. Harrington, M. Ayub and P.I. Haris, 2005. A biomaterial based approach for arsenic removal from water "; *Environ Monit.*, 7: 279-282.

- Bodo, R., A. Azzouz and R. Hausler, 2004. Multicriteria approach for the selection and a rational use of aquatic plants for wastewater treatment", *Plant Sci.*, 166: 893-899.
- Center, T. D., 1994. Chapter 23. Biological control of weeds: Water hyacinth and water lettuce., pp: 481-521.
- El-Khaiary, M.I., 2008. Kinetics and mechanism of adsorption of methylene blue from aqueous solution by nitric-acid treated water-hyacinth", *Journal of Hazardous Materials*, 147: 28-36B.
- El-Sayed, M.E., A. Omar, M. Ibrahim and W.I. Abdel-Fattah, 2009. On the Structural analysis and Electronic Properties of Chitosan /Hydroxyapatite Interaction. *J. Comput. Theor. Nanosci.*, 6: 1663-1669.
- Gopal, B., 1978. *Water Hyacinth*. Elsevier, New York, NY, pp: 471.
- Ibrahim, M. and T. Scheytt, 2007. Increasing the ability of Water hyacinth for removing Cadmium", Second International Congress on Environmental Planning and Management, TU-Berlin, Berlin, Germany, 5-10 Aug., 231-234.
- Ibrahim, M. and M. Abd-El-Aal, 2008. Spectroscopic study of Heavy Metals Interaction with Organic Acid. *Int. J. Environment and Pollution.*, 35(1): 99-110.
- Ibrahim, M., A.J. Hameed and A. Jalbout, 2008. Molecular Spectroscopic Study of River Nile Sediment in the Greater Cairo Region. *Applied Spectroscopy*, 62(3): 306-311.
- Ibrahim, M., A.A. Shaltout, M. Soyak, A.F. Jalbout and D-E. Kamal, 2009. Removal of COOH, Cd and Pb using water hyacinth: FTIR and Flame atomic absorption study. *J. Iran. Chem. Soc.*, 6(2): 364-372.
- Ibrahim, M., O. Kühn, and T. Scheytt, 2009. Molecular Spectroscopic Study of Water Hyacinth Dry Matter. *The Open Chemical Physics Journal.*, 2: 1-6.
- Ibrahim, H.S., M.A. Ibrahim and F.A. Samhan, 2009. Distribution and bacterial bioavailability of selected metals in sediments of Ismailia Canal, Egypt. *Journal of Hazardous Materials*, 168: 1012-1016.
- Ibrahim, M. and O. Osman, 2009. Spectroscopic Analyses of Cellulose: Fourier Transform Infrared and Molecular Modelling Study. *J. Comput. Theor. Nanosci.*, 6: 1054-1058.
- Ibrahim, M., A-A. Mahmoud, O. Osman, A. Refaat and E.M. El-Sayed, 2010. Molecular Spectroscopic Analyses of Nano Chitosan Blend as Biosensor. *Spectrochimica Acta Part A.* 77: 802-806.
- Ibrahim, M. and Z. Al-Fifi, 2010. Mechanism of Pollution Control for Aquatic Plant Water Hyacinth. *The Open Spectroscopy Journal*, 4: 10-15.
- Ibrahim, M., R. Mahani, O. Osman and T. Scheytt, 2010. Effect of Physical and Chemical Treatments on the Electrical and Structural Properties of Water Hyacinth. *The Open Spectroscopy Journal*, 4: 32-40.
- Ibrahim, M., "Molecular Spectroscopic Study of Acid Treated Fenugreek Seeds", *Spectrochimica Acta Part A*. In Press.
- Liao, S.W., W.L. Chang, 2004. Heavy metal phytoremediation by water hyacinth at constructed wetlands in Taiwan", *J Aquat Plant Manage.*, 42: 60-68.
- Malik, A., 2007. Environmental challenge vis a vis opportunity: The case of water hyacinth. *Environment International.*, 33: 122-138.
- Roldán, G., 2002. Treating Industrial Wastes in Colombia. Using Water Hyacinth. *Water lines.*, 2: 6-8.
- Rosen, D., F.D. Bennett and J.L. Capinera. (eds.). *Pest Management in the Subtropics: Biological Control - A Florida Perspective*. Intercept Publ. Co., Andover, U.K. pp: 737.
- Shawky, S., M.A. Geleel and A. Aly. 2005. Sorption of Uranium by Non-Living Water Hyacinth Roots. *J Radioanal Nucl Chem.*, 265: 81-84.
- Vermoehlen, K., H. Lewandowski, H.-D., Narres and E. Koglin, 2000. Adsorption of polyacrylic acid on aluminium oxide: DRIFT spectroscopy and ab initio calculations. *Colloids and Surfaces A: Physicochemical and Engineering Aspects.*, 170: 181-189.
- Xia, H. and X. Ma. 2006. Phytoremediation of ethion by water hyacinth (*Eichhornia crassipes*) from water. *Bioresource Technology*, 97: 1050-1054.