Removal of COOH, Cd and Pb Using Water Hyacinth: FTIR and Flame Atomic Absorption Study

M. Ibrahim[a], A.A. Shaltout[a], D.E. Atta[a], A.F. Jalbout[b] and M. Soylak[c]

[a]*Spectroscopy Department, Physics Division, National Research Centre, El-Behooth Street, Dokki, Cairo, Egypt.*
[b]*Institute of Chemistry, National Autonomous University of Mexico, Mexico City, MX*
[c]*Erciyes University, Fen-Edebiyat Faculty, Department of Chemistry, 38039, Kayseri-Turkey*

In the present work both FTIR and Flame AAS were jointly used to investigate the uptake of pollutants by the aquatic plant water hyacinth. The plant was immersed alive in synthetic standard solutions containing acetic acid up to 0.40 M for 19.0 h. Then it was immersed in 0.10 M acetic acid for different periods of time up to 210.0 h. Later on, both the acetic acid treated beside non treated ones was immersed separately in 1.0, 3.0 and 5.0 mg l^{-1} concentrates derived from Cd and Pb up to 240.0 h. The obtained results demonstrate the capability of the plant to remove both organic and inorganic pollutants. It is recommended that the plant be used to remediate Pb and Cd as well as other organic pollutants containing COOH. The results also indicate that the selectivity for Pb is higher than that of Cd. Additionally, pentahydrated divalent metal acetate model is presented to describe the coordination of the divalent metal ion with the acetic acid.

INTRODUCTION

Water hyacinth, an aquatic plant, flourishes in Egypt as well as other tropical and subtropical countries [1]. The construction of river control mechanisms brought about several ecological changes in the Nile system including the growth and spread of plants in almost all the aquatic habitats of this region [2]. The phenomenon of pollutant uptake was discovered many years ago by several researchers [3-6]. Addressing such issues continues to be a topic of major importance in many scientific research programs [7-9].

On the basis of our previous work, atomic emission spectroscopic methods were conducted to determine the levels of Cu, Pb and Ni in the water hyacinth root [10]. These levels

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*Corresponding author. E-mail: ajalbout@u.arizona.edu

of heavy metals in the water hyacinth beside other metals were measured seasonally along the Nile River by using atomic absorption spectroscopy [11]. The electrical properties were used to investigate the behavior of the metal ions in the plant through the variation of temperature and frequency characteristics [12].

The possible uptake of COOH by water hyacinth, as well as its survival in the presence of COOH with different concentrations, have been demonstrated in this work. The results indicate that the plant plays an outstanding role as an organic structure decontaminator. Additionally, we identified its role as a partial source of pollution whereby the plant releases metal ions into the aquatic environment as well [13]. Humic acids isolated from the leaves, stems and roots of water hyacinth from the Nile Delta (Egypt) were identified by chemical and spectral analysis [14]. Results suggested that the

presence of humic acid in plants is actively related to their metal binding properties. The water hyacinth showed a potential to remove a phosphorus pesticide that has been labeled as ethion [15-16]. Water hyacinth, like other aquatic plants, has been evaluated for its capability in removing mercury from water [17] which can also serve as an anti-pollutant tool. Interestingly, water hyacinth appeared to be the most effective plant for removing mercury as well as cyanide [18]. It has been demonstrated that cyanide at 5.8 and 10.0 mg l^{-1} concentrations was completely eliminated after 23-32 h [19], which is important in trying to locate potential phyto-remediation plants.

In a recent article, we demonstrated that the water hyacinth could be used in its dry form after being subjected to COOH to mediate Cd from water [20]. In order to demonstrate that water hyacinth can be used not only as dry matter, but also in its normal conditions, we attempted to carry out the following experiment. Accordingly, water hyacinth was tested as a phyto-remediation tool in the removal of COOH, and subsequently Cd and Pb from synthetic solutions. Both FTIR and Flame AAS were jointly applied in order to explore the said potential.

THE EXPERIMENT

Sample Collection

Water hyacinth was collected from the Nile River in Cairo (Rod El-Farag) in October 2007, and cultivated in a special pool at the NRC (National Research Centre, Dokki, Cairo, Egypt) to carry out the necessary experiments.

Uptake Experiments

Synthetic standard solutions of 1.0, 3.0 and 5.0 mg l^{-1} concentrations containing Cd and Pb were prepared by diluting a 1000 mg l^{-1} standard, which was purchased from the Merck Corporation (Darmstadt, Germany). Acetic acid was obtained from the same company.

Water hyacinth was immersed separately in a synthetic acetic acid solution of 0.02, 0.04, 0.10, 0.20, 0.30 and 0.40 M respectively for 19.0 h. Furthermore, the plant was immersed in 0.10 M acetic acid for different periods of time up to 210.0 h. Water hyacinth samples were collected after each immersion for FTIR analyses.

Water hyacinth was immersed in 0.10 M acetic acid for 210 h, and then in solutions containing 1.0, 3.0 and 5.0 mg l^{-1} Cd and Pb respectively. Water samples were collected at 0.5, 1.0, 2.0, 4.0, 12.0, 39.0, 139.0 and 240.0 h, respectively.

For the purposes of comparison, water hyacinth (without immersion in acetic acid) was immersed in solution containing 1.0, 3.0 and 5.0 mg l^{-1} Cd and Pb respectively. Water samples were collected at 0.5, 1.0, 2.0, 4.0, 12.0, 39.0, 139.0, 240.0 h, respectively.

All the uptake experiments above were carried out using triplicate water hyacinth samples.

Sample Preparation

Plants were washed with tap water followed by double distilled water, then divided into two parts namely, root and shoot, which were dried at 65 ºC for 48 hours. Both plant parts were weighed separately (as 1% w/w) with KBr to be ready for FTIR measurements.

Water samples were acidified before the appropriate analyses with flame atomic absorption spectroscopy.

Instrumentation

The Fourier Transform Infrared Spectrometer JASCO FTIR 300 E. (in the range of 400-4000 cm^{-1}) was applied for elucidating the molecular structure of the studied samples. The Varian SpectrAA220 atomic absorption spectrometer was used to determine water hyacinth uptake for the Cd and Pb metal species. The calibrations of Cd and Pb were performed at integration and peak area absorbance modes and measuring time 6 and 8 s, respectively. The necessity of suitable absorbance modes in AAS has been addressed elsewhere [11,20-25]. The oxidant rate used was 4.5 l min^{-1}, the fuel rate (C_2H_2) was 1.5 l min^{-1}, both of which are the optimal rates in the Flame AAS spectroscopy for Cd and Pb [23]. Table 1 illustrates the optimum operating conditions.

RESULTS AND DISCUSSIONS

Uptake of COOH

Water hyacinth was immersed in different molarities of acetic acid to study the COOH uptake. The plant was immersed in acetic acid with 0.02, 0.04, 0.10, 0.20, 0.30 and 0.40 M, respectively. Figure 1 presents the FTIR spectra of

Table 1. The Operational Optimal Conditions for Measuring Cd and Pb Using Flame Atomic Absorption Spectroscopy

		Optimal conditions			
Metal	Absorbance mode	Wavelength (nm)	Measuring time (s)	Slde width (nm)	Current (mA)
Cd	Integration	228.8	6	0.5	4
Pb	Peak area	217.0	8	1.0	5
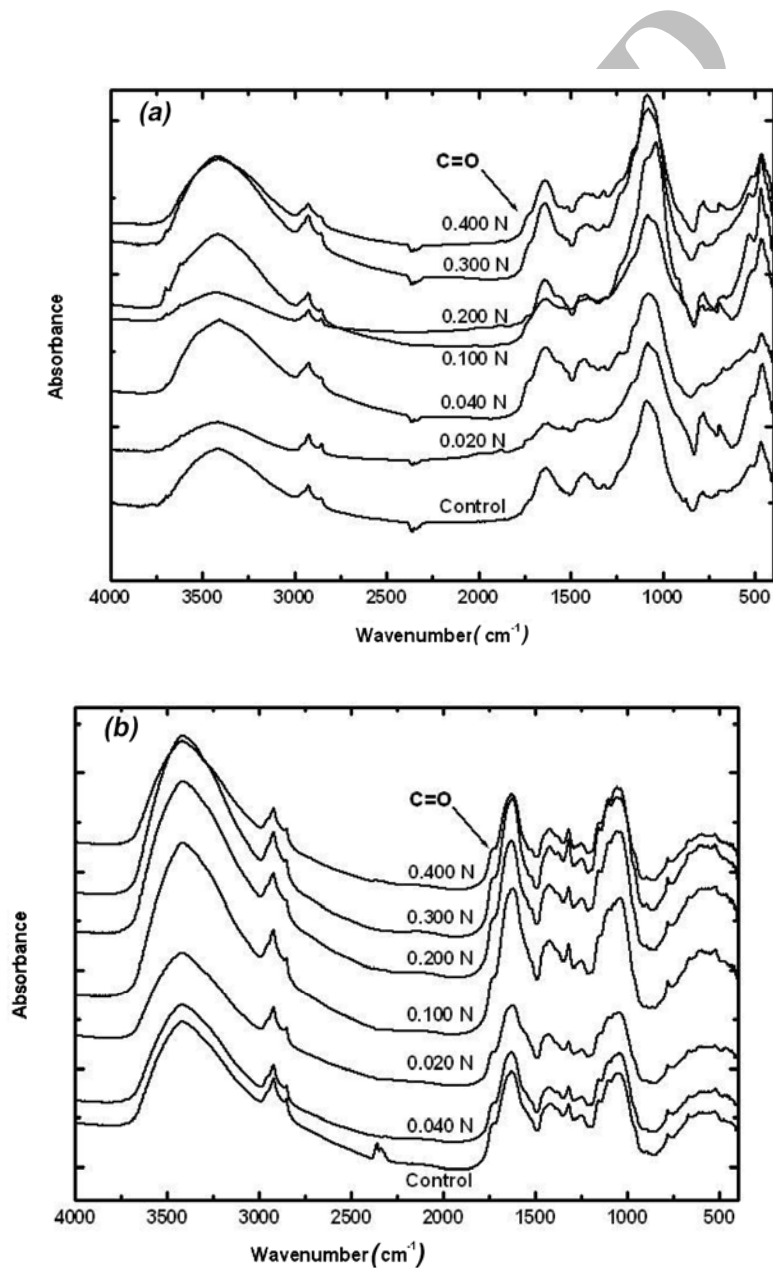
Fig. 1. FTIR spectrum of water hyacinth (a) root, and (b) shoot samples which were immersed in acetic acid with different moralities at 19.0 h.

both the water hyacinth root and shoot. The effect of the acetic acid in the FTIR spectrum is explained. The OH band of water is observed at 3388.3 cm^{-1}, and the CH (of CH$_2$) and CH$_3$ bands appear at 2922.6 and 2852.2 cm^{-1}, respectively. The stretching band of C=O (which is the characteristic band of carboxyl group) appears at 1738.4 cm^{-1}. Both the symmetric and asymmetric bands of COO arise in this spectrum at 1640.4 cm^{-1} and 1590.0 cm^{-1}, respectively as a result of metal carboxylate interactions, and then the C-O of CHO is located at 1516.7 cm^{-1}. The OH frequency which is observed at 1422.2 cm^{-1} may arise from phenolic compounds. The last part of the spectrum could be attributed to the metal oxides due to their relevant position in relation to the other frequencies. The spectra indicate the presence of C=O (the characteristic band of COOH) which arises from the uptake of acetic acid by the plant. Table 2 presents the ratio of C=O of each of the samples relative to the control in order to quantitatively describe the uptake of COOH. Results indicate that the ratio of C=O increases, going from 0.01 M to 0.10 M; then decreases at 0.20 M (while increased in shoot at the concentration), and subsequently increases up to 0.40 M. This indicates that the decrease in the root ratio stems from the possible transport from the root to the shoot at a 0.20 M solution of acetic acid. It also indicates that water hyacinth could be used to mediate organic structures that contain COOH group from the wastewater.

Figure 2 presents the water hyacinth immersed in 0.10 M at different times. Table 3 presents the results of the C=O ratio of the sample relative to the control as mentioned above to correlate the uptake of the plant quantitatively. The uptake is increased in the first 1 h at which point it comes to a maximum value at 38 h. The high uptake of the acetic acid at such short times suggests that the plant could be used successfully as a good phyto-remediation tool to remove organic pollutants (mainly containing COOH) from the aquatic environment.

Interaction between Divalent Metal Ions and COOH

In order to evaluate the relationship between COOH acid and the existing heavy metals, a model of the different possible interactions between the metals and acetic acid is presented. In our previous work [26-27], it was demonstrated that acetic acid can be chosen as a model system to base our

Table 2. Relative Absorbance Ratios of (C=O$_{Sample}$/C=O$_{Control}$) for Water Hyacinth at Different Acid Concentrations at 19 h

Acid concentrations (M)	Shoot	Root
0.02	0.796	1.182
0.04	0.812	1.355
0.10	0.997	1.552
0.20	1.066	1.020
0.30	1.001	1.351
0.40	0.857	1.411

calculations on. Using the B3LYP/LANL1DZ quantum mechanical method [28-30], the above-mentioned model of interaction is represented in Fig. 3. In the case of a heavy metal in water, the metal is surrounded by an excess of water molecules. After performing molecular modeling calculations, it was found that each metal ion shows an octahedral arrangement with coordinated waters attached to it. The interaction between acetic acid and each divalent metal ion (Cd and Pb) occurs via hydrogen bonding of the COOH. Thus, the existence of COOH attracts divalent metals by the electrostatic potential force that creates a relatively strong attraction between the species as our calculations suggest. It is worth mentioning that the hexahydrated metal ion became pentahydrated as the COOH is attracted to the metal ion instead of a water molecule. Furthermore, this interaction leads to a shift in the characteristic band of COOH (C=O). In our previous work the shift arising from Pb and Cd coordination to the COOH leads to shifts to around 1640.0 cm^{-1}, respectively. Smith [31] pointed out that this shift can be attributed to the fact that carboxylic group changes into metal carboxylate as a result of the proposed metal coordination.

Removal of Cd and Pb from Water

Water hyacinth already subjected to acetic acid at 0.1 M (210 h) was subsequently subjected to Cd and Pb with different concentrations namely 1.0, 3.0 and 5.0 mg l^{-1}. The results will be compared with a plant which is not subjected to acetic acid to assess the role of COOH in the metal uptake and
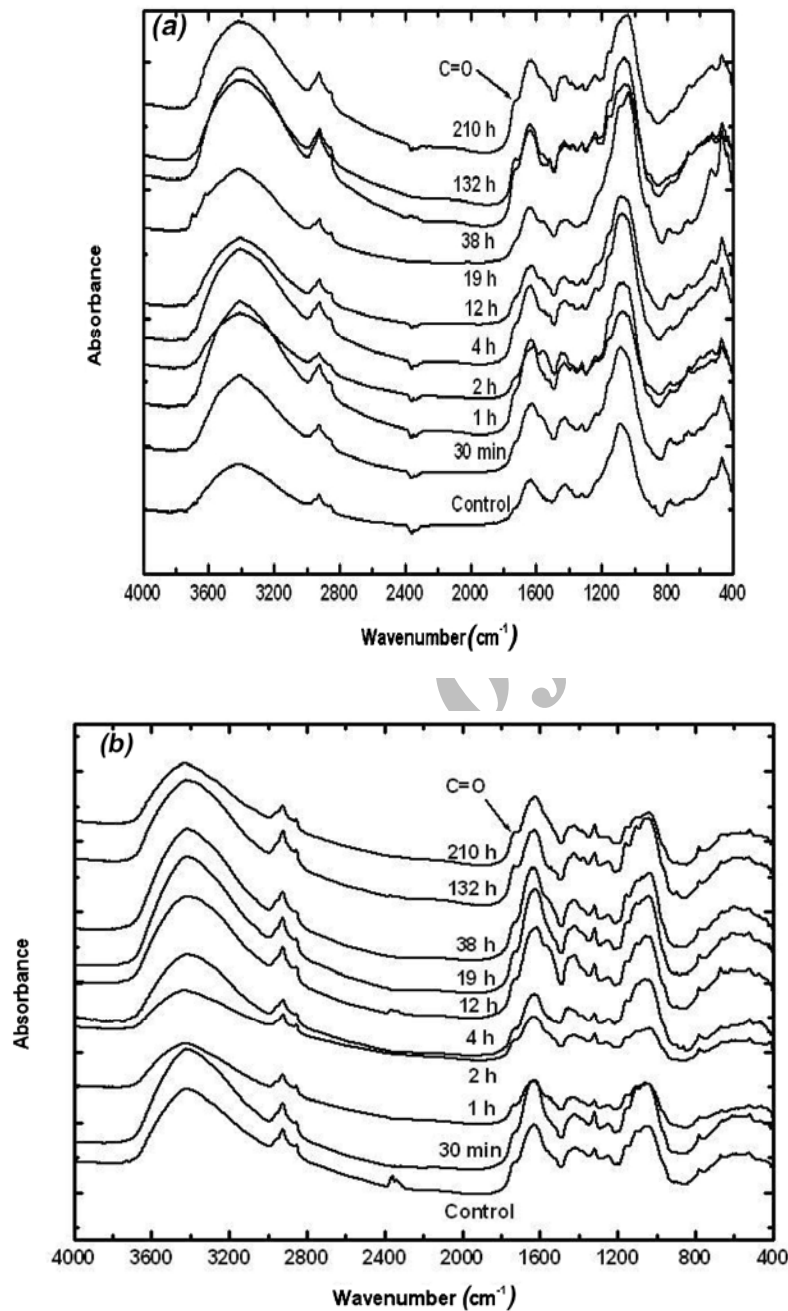
Fig. 2. FTIR spectrum of water hyacinth (a) root, and (b) shoot samples that were immersed in 0.10 M acetic acid at different times.

the possibilities of using the plant for mediating both organic and inorganic pollution simultaneously.

Figure 4 depicts the uptake rate of Cd for both immersed and non-immersed plant in COOH. In the case of non-

immersed plant, the phenomenon of uptake is more profoundly distinguished for the 1.0 mg l^{-1} solution especially in the first 50 h after which it becomes stable up to 240 h. From our experimental observations, the plant uptake of Cd

Table 3. Relative Absorbance Ratios of ($C=O_{Sample}/C=O_{Control}$) for Water Hyacinth which was Immersed in 0.10 M Acetic Acid for Different Times

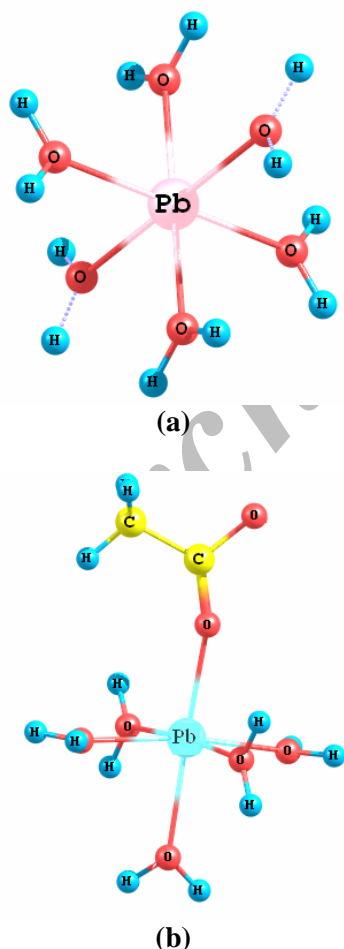| Time (h)	Shoot	Root
0.5	0.955	1.399
1.0	1.074	1.605
2.0	0.870	1.215
4.0	0.813	1.426
12.0	0.933	1.282
19.0	0.997	1.552
38.0	0.948	2.042
132.0	1.139	1.612
210.0	1.133	1.917

Fig. 4. Uptake of Cd at 1.0, 3.0 and 5.0 mg l^{-1} synthetic solution in the case of acetic acid previously uptake as well as without acetic acid (dashed lines).

(a)

(b)

Fig. 3. Model structure of (a) Hexahydrated divalent metal, and the (b) Interaction between hexahydrated divalent metals and the acetic acid through COOH.
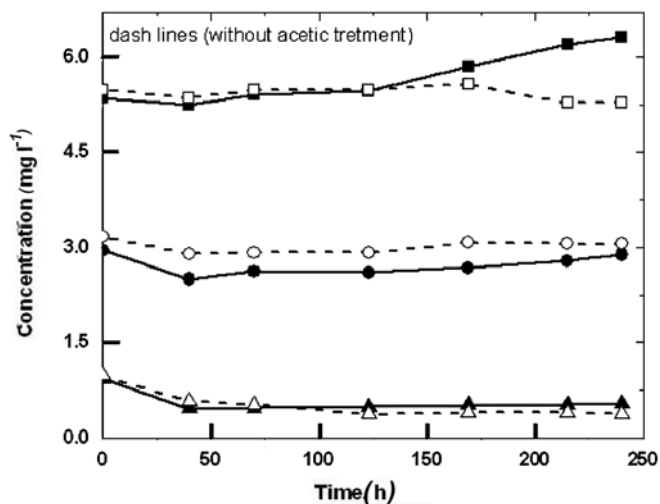
greatly decreases at a solution concentration of 5.0 mg l^{-1}.

On the contrary, for the plant which is previously used for uptake of 0.10 M acetic acid the results indicate that in the case of the 1.0 mg l^{-1} solution there is an increase in metal uptake by the plant within the first 50 h which stabilizes up to 240 h as previously mentioned. The uptake rate of the plant is lowered (relative to the control plant) at a solution concentration of 1.0 mg l^{-1}. The availability for Cd removal is increased in the case of 3.0 mg l^{-1}, while at 5.0 mg l^{-1} the uptake disappears and the level of Cd increases in the collected water which indicates that Cd may release itself from the plant. Generally speaking, the uptake rate for each plant (immersed and non-immersed in COOH) is comparable to the other.

Figure 5 shows the removal of Pb from water containing 1.0, 3.0 and 5.0 mg l^{-1} concentrations. As the data show the plants' uptake is greatly increased during the first 19 h. Generally speaking, the plant used previously for COOH uptake could remove Pb, but was relatively low when compared with the plant which was not immersed in acetic acid. On the whole, water hyacinth under study is considered as a selective agent for Pb as compared with Cd. Furthermore, the uptake of Pb by control plant is much higher than that of the plant which was previously used for COOH uptake.
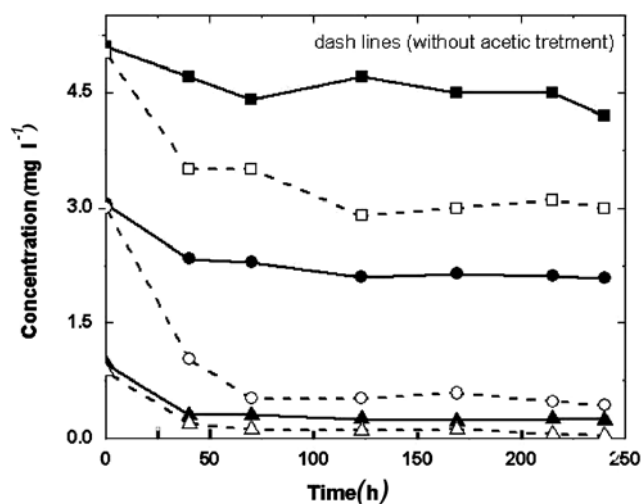
Fig. 5. Uptake of Pb at 1.0, 3.0 and 5.0 mg l^{-1} synthetic solution in the case of acetic acid previously uptake as well as without acetic acid (dashed lines).
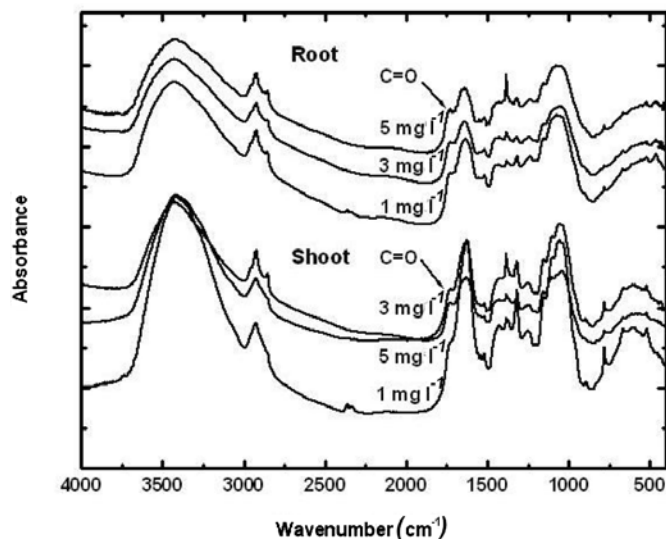

Fig. 6. FTIR spectra of water hyacinth roots and shoot samples at a constant time with the existence of Cd, Pb and after using the plant for 0.10 M acetic acid uptake.

Figure 6 shows the FTIR spectra of the water hyacinth which was used for uptake of COOH (0.10 M for 210 h) and then Cd and Pb (1.0, 3.0 and 5.0 mg l^{-1} for 240 h). The FTIR

Table 4. Relative Absorbance Ratios of (C=O$_{Sample}$/C=O$_{Control}$) for Water Hyacinth which was Immersed in 0.10 M Acetic Acid and with Metals (Cd and Pb) for 19 h

Concentration (mg l^{-1})	Shoot	Root
1	0.861	0.962
3	1.143	0.893
5	1.032	0.839

spectra indicate the presence of C=O as a result of COOH uptake. Furthermore, the plant is able to remove Cd and Pb. The increasing rate of uptake in a longer time indicates the ability of the plant to survive in different circumstances and/or its capability to remove structures containing COOH whatever the time and/or the concentrations of these structures.

The results in Table 4 show that, there is a decrease in the C=O ratios of the root as compared with that of the shoot. This indicates that a transport of metals from root to shoot took place.

There was an increase in the band intensities at 1640.4 cm^{-1} and 1590.0 cm^{-1} which corresponds to symmetric and asymmetric stretching modes of metal carboxylate. This arises from the possible interaction between Cd, Pb and COOH. The proposed statement is in good agreement with the presented model of pentahydrated divalent metal acetate. Also, we must note that the presence of COOH allows for increased removal of divalent metals (especially Cd and Pb) as well as organic pollutants containing COOH. Therefore, water hyacinth could be used efficiently to remove organic and/or inorganic pollution from the aquatic environment. The increase of the C=O relative absorbance in shoot (for plant which mediate COOH) indicates the transport of metals from the root to the shoot. Therefore, water hyacinth could be used directly to remove the above-treated metals from wastewater efficiently. In order to further achieve the maximum benefits of plant uptake, we may treat the plant with acetic acid at low concentrations (for a minimal quantity of time) and reuse it to increase its capacity for metal uptake.

It was assumed that the uptake of COOH enhances the ability of the plant to remove metals from aquatic environment. This was proven in our previous work [20]

wherein acetylated water hyacinth in its dry form was used to mediate Cd from water. In the present work the uptake is slightly changed or not changed at all as the plant was used alive after being subjected to acetic acid with high concentrations. This may be due to the fact that the plant in dry matter is only influenced by the chemical processes so that the existence of COOH enhances the uptake according to the given model. Alternatively, when the plant is used alive it is influenced by both chemical and biological processes so that something like selectivity takes place. Accordingly, the effect of the acetic acid upon the plant is elucidated to clarify the fate and transport of pollution in the plant under the influence of both organic and inorganic pollutions.

CONCLUSIONS

It could be recommended that the plant be cultivated in numerous beds where the wastewater could enter each bed for a short period of time at which point the plant could remove organic pollution as well as Cd, Pb efficiently. Based on the presented model, treating the organic pollution with 0.10 M acetic acid for a short time (19 h) may in turn increase the ability of the plant to remediate pollutant after converting organic pollution into organo-acetate structures. Also, acetic acid at 0.20 M solutions could be used to transport metals from root to shoot. This increases the ability of root to metal uptake as well as an increase in the life of remediation for the plant. Such an attribute is of importance, and warrants further study by the scientific community in order to alleviate the quantity of pollution in important bodies of water. Findings of this study combined with those of our previous work [20] indicate that acetylated water hyacinth in its dry form could be used in the same beds to enhance the uptake of Cd and may be other heavy metals as well.

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