Mechanism of Pollution Control for Aquatic Plant Water Hyacinth

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Abstract: The aquatic plant water hyacinth is a powerful tool for mediating pollution from aquatic environment. PM3 semiempirical method and FTIR spectroscopy was used to predicate the mechanism of pollution control. First the plant is subjected to acetic acid 0.1 M for 19 hours. FTIR proves that the plant is cellulose like material. Furthermore, the acetylated plant is looks like cellulose acetate. The mechanism of acetylation is tested using PM3 method. CH_3COOH is interacted with OH of CH_2OH by two ways. The first is through H-bonding of CH_3 the second is through the interaction of the H-bonding of COOH. The mechanism of divalent metal removal was such that Cd as an example is coordinated with acetylated plant either through two OH of CH_2OH or through two COOH attached with CH_2OH.

Keywords: PM3, FTIR, acetylation, cellulose and water hyacinth.

INTRODUCTION

By 2025 Egypt as well as Arabic world is expected to suffer from water scarcity. That is why it is a must to manage the existing water on one hand and study other possible strategies to increase water budget on the other [1]. One of the possible solutions is reuse of the sewage water, which could solve part of the water demand and/or compensate for water shortage in the near future. One of the limitations is uncontrolled discharge of wastewater directly to urban systems without adequate treatment. This discharge contains several pollutants, mainly heavy metals. This in turn makes the process of sewage water treatment more expensive and needs extra efforts. One of the recommended methods to overcome this problem is utilizing the plant (phytoremediation) and/or bacteria (bioremediation) for treatment. The aquatic plant water hyacinth is growing abundantly in tropical and subtropical regions of the world. The phenomena of pollution control by this plant were observed earlier [2-4]. Nowadays, the plant is used extensively as a phytoremediation tool [5-8]. The plant was a topic of our previous work [9-12]. Furthermore, semiempirical methods were a subject of our research work for many systems and molecules whereas fast results are needed to describe their behavior [13-15]. Many properties such as electronic, structural as well as spectroscopic properties were investigated with these methods [16, 17].

Based on our previous modeling as well as FTIR studies, the present paper is conducted and point out the possibility of mediating heavy metals by aquatic plant. The plant was treated with acetic acid and then used as dry matter. The mechanism of removal is studied using molecular modeling technique based on experimental FTIR spectroscopy measurements. For verification the dry acetylated plant is immersed in 2mg/l Cd solution to test its ability for metal mediation.

FTIR INVESTIGATION

The water hyacinths were collected from the Nile (Cairo-Egypt), and then subjected to acetic acid up to 0.1 N for 19.0 hours. The plant is divided into root and shoot, washed thoroughly then dried at 65 ^oC till constant weight.

Cellulose standard and cellulose acetate was purchased from Aldrich Chemicals.

Each sample (root, shoot and cellulose) was mixed with KBr (1% W/W) and pressed in pellets to be ready for FTIR measurement.

One gram of shoot and root was separately immersed in water containing 2.0 mg/l Cd. Water samples were collected at 0.0, 1.0, and 2.0, then measured using Flam Atomic Absorption Spectrometer (FAAS) [10, 12].

INSTRUMENTATION

The FTIR spectra were collected using Fourier Transform Infrared Spectrometer JASCO, FTIR- 300 E., in the range of 400 to 4000 cm^{-1} at Spectroscopy Department, National Research Centre, Egypt.

NovAA 400 Jena Flame Atomic Absorption Spectrometer, at Geochemical Laboratory, Technical University of Berlin, Germany was used for the determination of Cd. The operational conditions were 3.0 mA lamp current, 228.8 nm spectral line, 8.0 mm burner height, 5.0 s measuring time, using air acetylene flame [10, 12].

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CALCULATION DETAILS

Molecular modeling calculation was carried out on a personal computer performed using quantum mechanical methods as implemented with the MOPAC 2002 Version 1.33 CAChe Program (by Fujitsu) [18]. Cellulose model molecule is consists of 6 units β-D Glucose 1-4 linkage as seen in Fig. (**1a**). Other four model molecules in Fig. (**1**) are representing the possible acetylation of cellulose and the possible coordination of Cd with cellulose. The geometry of each structure is optimized by PM3 semiempirical method [19, 20]. Vibrational frequencies are then calculated at the same level of theory. Cellulose model molecule was consists of 6 unit β-D

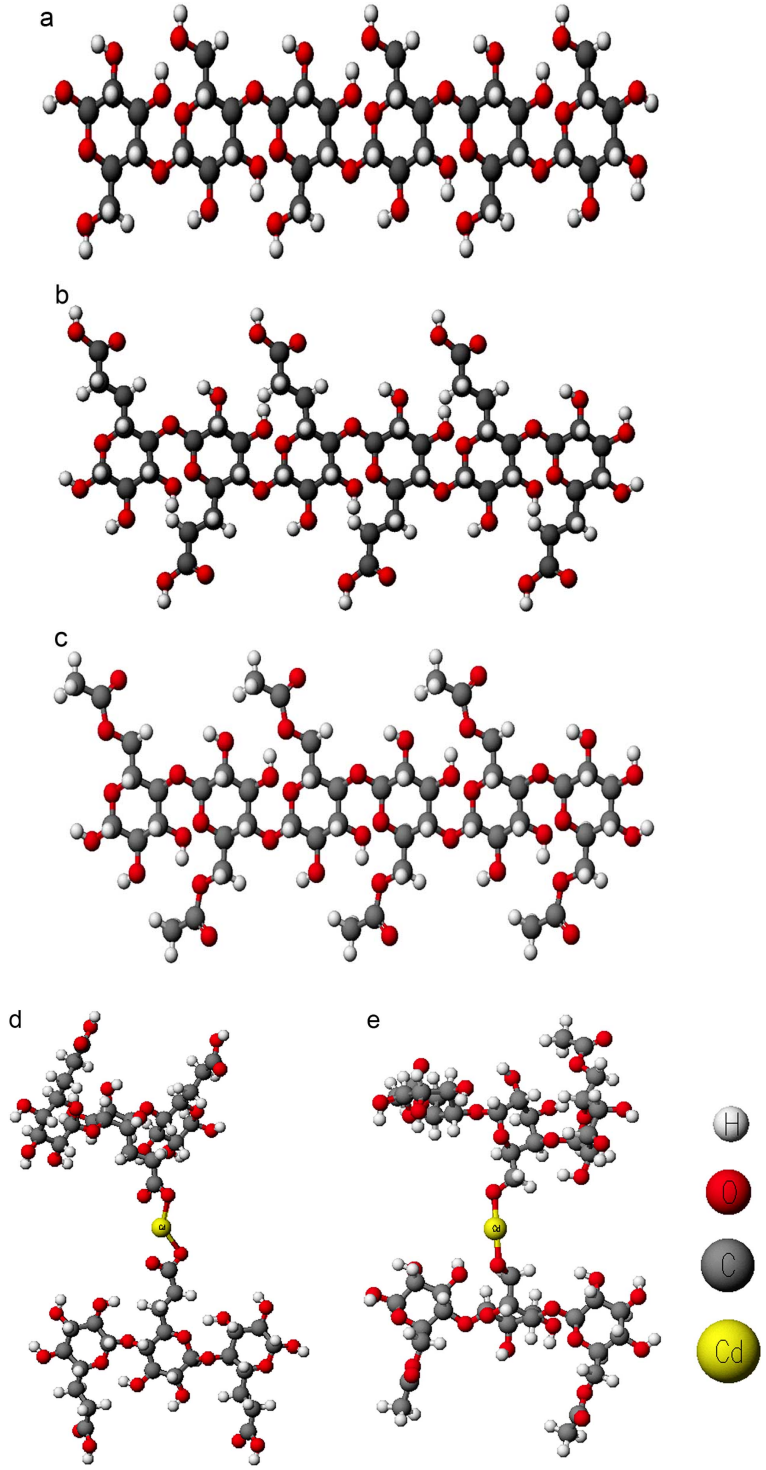

Fig. (1). Optimized PM3 structures of **a**- Cellulose 6 units (Cel6) each unit is a β-D Glucose 1-4 linkage, **b**- Acetylated cellulose whereas acetic acid is interacted with the OH of CH_2OH through one H-atom of the CH_3, **c**- Acetylated cellulose whereas acetic acid is interacted with the OH of CH_2OH through the H-atom of the COOH, **d**- Cd is interacted with cellulose acetate through the COOH which is attached with CH_2OH and **e**- Cd is interacted with cellulose acetate through OH of CH_2OH.

Glucose 1-4 linkage as seen in Fig. (**1a**). Other four structures representing the acetylation of cellulose and the coordination with Cd are also indicated in Fig. (**1**).

RESULTS AND DISCUSSIONS

FTIR Assignment of Cellulose

FTIR absorption bands for standard cellulose are indicated in Fig. (**2**). The assignment is first aided by the model program and agreed with that obtained by Bouchard and Douek [21], also with our previous findings [22].

The spectrum indicates the presence of OH stretching of water at 3348 cm^{-1}. The CH symmetric stretching vibration of CH_2 is regarded around 2900 cm^{-1}. The C-O vibration arises at 1640 cm^{-1}, while CH_2 vibration has another band at 1430 cm^{-1}. The split band CH_3 umberlla mode at 1372 ~ 1336 cm^{-1}. Then C-CH vibration at 1318 cm^{-1}. It is stated that, the characteristic bands of cellulose are mainly remarked around 1000~1200 cm^{-1} [21]. The band near 1160 cm^{-1} is representative of the antisymmetric bridge stretching of C-O-C groups in cellulose and hemi-cellulose, and the band near 1318 cm^{-1} could be ascribed to CH_2-wagging vibrations in cellulose and hemi-cellulose. The band at 895 cm^{-1} is attributed to β-linkages, especially in hemicelluloses which in a good agreement with Michell [23].

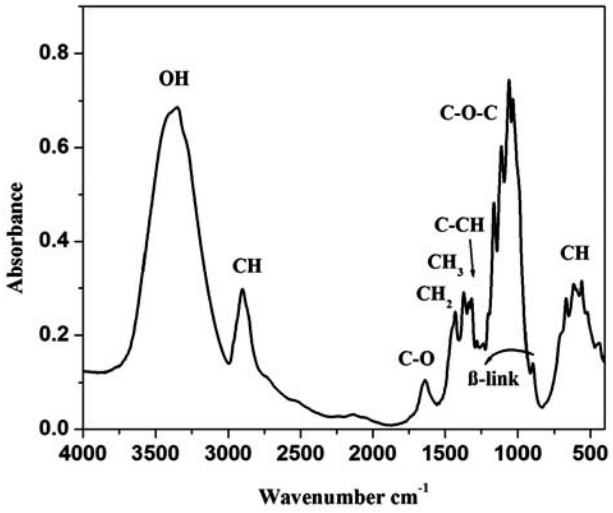

Fig. (2). FTIR absorption spectrum of standard cellulose.

WATER HYACINTH IS CELLULOSE LIKE MATERIAL

Fig. (**3**) indicates the FTIR absorption spectra of water hyacinth root and shoot in comparison with that of standard cellulose as well as cellulose acetate. The spectra indicate that water hyacinth is cellulose like material or a structure containing a majority of cellulose fibers. Furthermore, treating the plant with acetic acid 0.1 M for 19 hours indicate the presence of C=O and no bands for the unreacted acetic acid are regarded. This may lead to a conclusion that acetic acid makes each plant part behaves like cellulose acetate. The higher C=O band intensity corresponding to cellulose acetate was higher as compared with that for acetylated plant. This reflects the unacetylation of all cellulose of the plant. The appearance of C=O indicates the ability for water hyacinth to mediate organic structures which contains COOH. This is in a good agreement with our previous findings [11]. Furthermore the existence of COOH in the plant provides further ability for the plant to mediate heavy metals. Accordingly we try to describe the fate of COOH in the plant in order to maximize the use of the plant in pollution control.

FATE OF COOH THROUGHOUT CELLULOSE

In our previous modeling work we indicate that COOH could replaces one of the abundant OH in cellulose [12, 22]. Even we found a favorable cites based on binding energy. Furthermore COOH could interact with OH of CH_2OH of cellulose to form ester and water molecule.

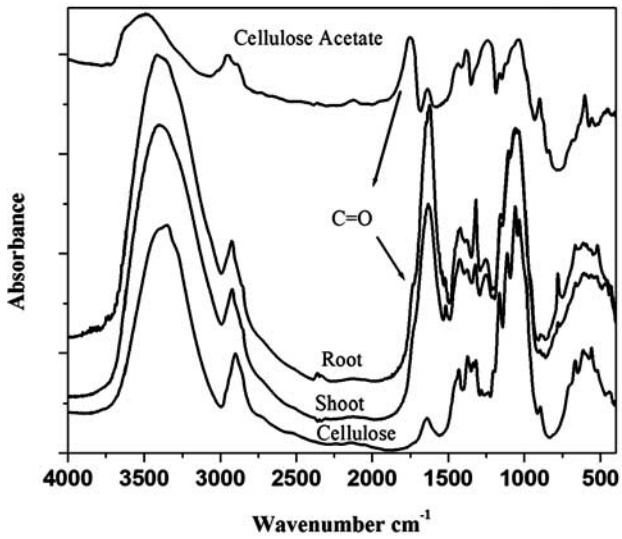

Fig. (3). FTIR absorption spectra of water hyacinth root and shoot in comparison with cellulose and cellulose acetate.

The mechanism was tested upon one cellulose unit as β-D Glucose 1-4 linkage. In the present work we apply semiempirical PM3 method for cellulose up to 6 units. For each structure the optimized geometry is found then vibrational frequencies were calculated to confirm the occurrence of each structure. COOH is interacted with cellulose through OH of CH_2OH forming two schemes. The first scheme, the hydrogen atom of CH_3 is interacted with the OH of CH_2OH. This scheme is termed Cel-CH_2COOH; in this scheme hydrogen bonding of acetate is available for mediating heavy metals. The second scheme is the hydrogen atom of COOH is interacted with the OH of CH_2OH. This scheme is termed Cel-OOC-CH_3; in this scheme hydrogen bonding OH of CH_2OH is available for mediating heavy metals. Fig. (**4**) presents the spectra of acetylated cellulose. A decrease is noticed in the OH transmittance of OH of CH_2OH as it is responsible for interaction with acetic acid. A split in the CH band is regarded as the existence of CH_2 and of CH_3. C=O is appeared as a result of acetylation. CH of CH_3 is appeared corresponding to Cel-OOC-CH_3.

MEDIATION OF DIVALENT HEAVY METALS

Mediation of heavy metals is an environmental challenge. We try to mediate Cd using acetylated plant and/or

cellulose acetate through the investigated PM3 scheme which indicated in Fig. (**1e** and **1f**). Cd is assumed to interact with two acetylated cellulose units. Either through two OH of CH_2OH in case of Cel-OOC-CH_3 or through H of COOH in case of Cel-CH_2COOH.

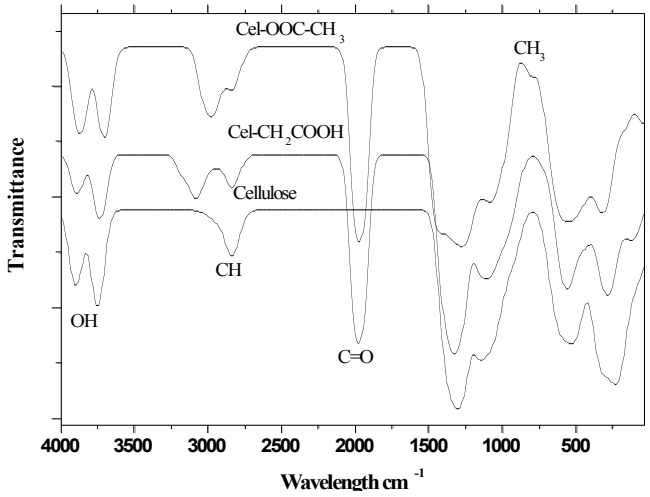

Fig. (4). Calculated PM3 spectra of cellulose 6 units as compared with acetylated cellulose whereas in case of Cel-CH_2COOH; acetate is interacted with CH_2OH through H-bonding of CH_3 of the acetic acid. In case of Cel-$OCCH_3$ the H-bonding of the COOH is interacted with the OH of CH_2OH.

Fig. (**5**) presents the calculated spectra of Cd interaction with two acetylated schemes. As far as Cd is coordinated with OH of CH_2OH a small band is raised around 1700 cm^{-1}. As Cd is coordinated with COOH a strong band of Cd carboxylate arises around 1700 cm^{-1}. To describe the property of each Cd coordination both the total dipole moment and the binding energy of interaction based on highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). These values are calculated and listed in Table **1**. Total dipole moment reflects the reactivity of each structure with the surrounding molecules [24, 25].

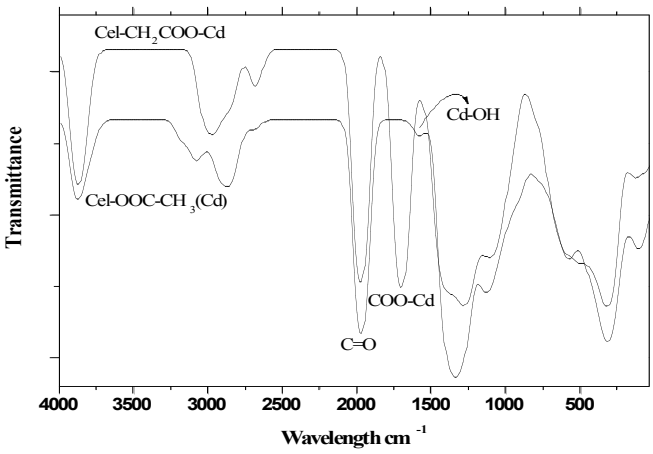

Fig. (5). Calculated PM3 spectra of two acetylated cellulose interacting with Cd as Cel-CH_2COOCd, and Cel-OOC-CH_3(Cd).

As seen in Table **1** the total dipole moment is 9.151 debye corresponding to cellulose. Then slightly decreases corresponding to Cel6-CH_2COOH to be 8.358 debye. As far as this acetylated structure is coordinated with Cd the corresponding dipole moment is decreased to be 2.707 debye. This indicates that Cd found a stable structure within the cellulose units with less ability to further interact with the surrounding molecules. Another scheme of acetylation is Cel6-OOC-CH_3 has 5.844 debye. Subsequently became 6.829 debye corresponding to Cd interaction with Cel6-OOC-CH_3 this indicate that this structure could interact further with the surrounding molecules. Even Cd could remobilized from the structure back to the environment leaving cellulose as high as before 9.151 debye. From this point of view acetylation of cellulose through H of CH_3 (CH_3COOH) is more important than that thorough COOH of (CH_3COOH). This could produce stable structure while other scheme of acetylation coordinates with Cd with possible remobilization back toward the surrounding aquatic environment. Regarding the calculated binding energy indicate that, acetylation through Cel6-CH_2COO-Cd requires less energy than that of Cel6-OOC-CH_3. While coordination with the second acetylated scheme requires less energy than the first. This revealed that acetylation could happen directly through the OH of CH_2OH. Collecting the calculated data together, one could observe that acetylation of cellulose enhances its ability to mediate heavy metals.

VERIFICATION OF THE MODEL

Regarding the spectra in Fig. (**3**) it is clear that C=O in the plant enhances its usage to mediate organic structures containing carboxyl group like organic acid and some medical waste. Another attempt is tried to test the mediation of Cd from wastewater. A short term experiment were carried out and listed in Table **2**. Results indicate that treating the plant with 0.1 M of acetic acid and using it for short time as a dry matter enhances its ability to mediate Cd from aquatic environment which in a good agreement with our previous findings [12].

CONCLUSIONS

As far as water hyacinth treated with acetic acid it becomes as cellulose acetate and could be used as a useful tool for pollution control. The spectra of treated water hyacinth show no absorption bands in the region of 1840-1760 cm^{-1} which indicates that these samples are free of unreacted acetic acid anhydride. Furthermore, no bands were found at 1700 cm^{-1} which gives evidence that the treated samples are free of acetic acid by-products. These observations are in good agreement with previous results reported concerning the acetylation of cellulose [26, 27]. So that water hyacinth is a cellulose fiber or cellulose like material. The mechanism of acetylation is tried with PM3 method which indicates the possibility for acetic acid to interact with the OH of CH_2OH either through one of the H-bonding of CH_3 or the H-bonding of COOH. Calculated total dipole moment indicates that interaction through CH_3 could further mediate Cd with

Table 1. Calculated Total Dipole Moment (TDM) as Debye, and Binding Energy as e.V for Acetylated Cellulose and Cd Coordinated with Acetylated Cellulose

Structure	TDM (Debye)	Binding Energy (e.V)
Cellulose 6 units of β-D Glucose 1-4 linkage (Cel6)	9.151	12.048
Cel6-CH_2COOH	8.358	11.195
Cel6-CH_2COO-Cd	2.707	10.813
Cel6-OOC-CH_3	5.844	11.576
Cel6-OOC-CH_3 (Cd)	6.829	9.952

Table 2. Concentration of Cd as mg/l for Acetylated as well as Nonacetylated Water Hyacinth Root and Shoot

Time, Hours	Root (R)		Shoot (S)	
	Untreated	Treated	Untreated	Treated
0.0	0.1993	0.1993	0.1993	0.1993
1.0	0.2215	0.1033	01445	0.0932
2.0	0.1584	0.0953	0.1291	0.0918

possibility for remobilization while better stability of Cd remediation is assumed to be through the interaction with cellulose acetylated through H of COOH. Accordingly water hyacinth could be used extensively after acetylation and in the form of dry matter to mediate organic as inorganic pollution. As one uses the plant in dry matter; no affect upon oxygen content and light penetration through water which minimize or even eliminate the adverse impacts of water hyacinth to the surrounding environment. Furthermore, dry matter has small size then after accumulation of pollution could be incinerated in a special kiln.

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