Article

Cadmium Uptake, In Vivo Metastasis and Subcellular Environmental Response of Five Wetland Plants Using DFT Method

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Abstract: The main purpose of this study is to analyze whether Cd^{2+} affects the absorption of Ca^{2+} and Fe^{2+} by the roots of five wetland plants and the toxic mechanism of cadmium on the subcellular structure. Five wetland plant samples were collected from the constructed wetland in the upper reaches of the Yangtze River. Based on the experiment and density function theory (DFT), we measured the Cd^{2+} content in the root, stem, and leaf, the morphological dimensions of plants, and in the subcellular structure the electronic activity of Cd compound was calculated to describe the stability and activity of the products. In general, *Zephyranthes candida*, *Cynodon dactylon*, *Arundo donax*, and *Pontederia cordata* have distinct cadmium uptake characteristics, while *Phragmites communis* does not. The results indicated tolerance to cadmium in all but *Phragmites communis*, which was due to cadmium distribution through the process of transpiration and a mechanical interception. The simulation results showed that Cd^{2+} imposed no obvious inhibition on the absorption of Ca^{2+} and Fe^{2+} in plants, as the energy barrier of the process is about 1–3 eV. Cd^{2+} could improve the amount of pyruvate and glucose by 30% via *spd* orbital hybridization, making them more chemically reactive. At the same time, Cd^{2+} could replace Mg^{2+} in chlorophyll through a copper substitution reaction, making the electron energy of chlorophyll more concentrated. As a result, the valence-band electron at -40 eV was vacant. In conclusion, we determined that Cd^{2+} has no obvious inhibitory effect on Ca^{2+} and Fe^{2+} in root absorption and that Cd^{2+} could affect the properties of compounds of the subcellular structure and thus produce physiological toxicity.

Keywords: wetland plants; density functional theory (DFT); cadmium enrichment factor; cadmium transport coefficient; subcellular structure

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1. Introduction

Although cadmium is not an essential element for plant growth and development, it can be absorbed by plants through the root system and accumulate in the plant. The accumulation of cadmium would contaminate the food chain and threaten higher-level consumers and human beings [1–3]. Furthermore, cadmium is biologically toxic, as it can inhibit plant cell growth [4] and oxidative phosphorylation [5], as well as cause oxidative stress [6], affect photosynthesis [7], and damage subcellular structure and activity [8–10]. A previous work [11] showed that the upper reaches of the Tuojiang River in Southwest China was polluted by cadmium, while the water quality in the lower reaches was in good condition. The cadmium content in the upper reaches was $0.0909 \text{ mg} \cdot \text{L}^{-1}$, which greatly exceeded the requirements of China's national water quality standard of $0.005 \text{ mg} \cdot \text{L}^{-1}$. It could be inferred that the constructed wetlands along the Tuojiang River removed a large amount of available cadmium. Although a previous work [12] studied the role of constructed wetland in cadmium removal, in order to reveal the pathways of cadmium removal it is still of great importance to study the absorption and transport of cadmium by wetland plants.

Generally, cadmium uptake by plants involves the following processes: (1) root uptake, (2) transport from root to stem, and (3) transport from stem to leaf. The factors affecting cadmium uptake by roots mainly include soil pH, total soil cadmium, soil organic matter, root exudates, and tufted microbial exudates. As proposed by Teisser in 1977, cadmium exists in the environment in different states, such as an exchangeable state, a carbonate state, an Fe/Mn oxides state, an organic/sulfide state, and a residual state [13]. The exchangeable state generally refers to water-soluble cadmium salt, which has the strongest bioavailability. A high exchangeable cadmium content could be expected in soils with high total cadmium and lower pH [14]. Generally, the soil organic matter content leads to an increase in exchangeable cadmium content [15]. However, there is also evidence that increased soil organic matter content can lead to a decrease in available cadmium content [16]. Available cadmium content is mainly determined by the nature of soil organic matter [17]. For example, organic acids secreted by plant roots are beneficial for the increased availability of cadmium in soil [18,19]. The presence of tartaric acid can increase the content of available cadmium by 1.4–6.9 times [20]. Normal soil organic acids, including ethylenediamine tetra-acetic acid, citric acid, malic acid, and oxalic acid, can increase the proportion of available cadmium to total cadmium in soil [21,22].

Root exudates can increase the competitive absorption of ions in the environment, consequently promoting or inhibiting cadmium uptake. A study has shown that the transport efficiency of cadmium can be improved by the competitive occupation of calcium and iron absorption sites within the root system [23]. At the same time, research has also shown that the absorption capacity of iron and cadmium changes synchronously, indicating no competitive absorption [24]. Similar conditions have been reported for other essential metals, for instance, in wheat experiments it has been proven that there is no competitive absorption of zinc and cadmium [25]. In 2020, a study that showed the active addition of nutrients needed for rice, iron, and manganese found that both elements inhibited cadmium absorption by 9–65% [26]. However, their conclusions explain the inhibition from the aspect of transporter proteins rather than the absorption sites of root exudates. A review claims the divalent cations have the similar two stages of uptake process, the apoplastic and symplastic pathways [27]. Some results even found Fe could facilitate Cd uptake [28]. For the apoplastic pathway, the divalent cations compete for shared organic acid adsorption sites. Considering the distribution between different ions, the specific absorption energy and energy of complex can be calculated using density functional theory (DFT) to determine which heavy metal possesses an absorption advantage.

Generally, cadmium hyper-accumulators usually have developed roots and dense root hairs [29]. For example, a cadmium absorption capacity of $1800 \text{ mg} \cdot \text{kg}^{-1}$ was observed for *Thlaspi caerulescens*. The transport efficiency from root to stem is an important feature of hyper-accumulators, while the accumulation capacity of organic acids in plants determines the maximum accumulation amount of cadmium [30]. The xylem is the channel for cadmium transport from root to stem, with transpiration and root pressure dictating the transport rate of the process [31]. The transport of cadmium in the xylem and the accumulation of cadmium in the stem were accelerated under stronger transpiration and higher root pressure. When abscisic acid was used to inhibit the transpiration of plants, it was found that the concentration of cadmium in aboveground parts of plants decreased [32]. Once cadmium is accumulated in the stem, with the development of plants, cadmium will enter the phloem and be redistributed into various organs of the plants [33,34]. As the phloem is connected to important organs such as the flowers, leaves, and fruits, the presence of cadmium in the phloem could result in subcellular structural toxicity. Cadmium accumulation in subcellular structures mainly resulted in variations in morphological and physiological processes. Reduction in dry matter yield and leaf area shrinkage were reported [35–37] for morphological variations, and chlorophyll was reduced [38], photosynthesis and respiration were inhibited [39], and growth was slowed [40]. Cd uptake in basil seeds delayed the germination for 3–6 days [36]. High concentration of Cd contributes to the delayed growth rate, and it was speculated that Cd inhibits the absorption and transport of wa-

ter [41]. Tomato [42] and cucumber [43] have a decreased photosynthetic performance due to Cd uptake. For respiration, there is proof Cd could transport electrons to the electron donor [44]; therefore, it could seriously impede the normal respiration. Therein, some reaction products could trap cadmium in organelles, persistently interfering with normal physiological processes [45]. Similarly, the subcellular structure could affect the form and transport of cadmium. For example, the vacuoles of some cadmium hyper-accumulation plants can trap cadmium ions with malic acid [46]. Therefore, it is of great importance to reveal the active forms of the main organic compounds and cadmium in subcellular structures. To simulate the effect of cadmium ions on the subcellular structure, chlorophyll A and B are used to represent the chlorophyll environment, while glucose and pyruvate are used to represent the mitochondrial environment.

In order to further describe the interactions and performance changes of cadmium ions with plant metabolites, subcellular structure, and main components, density functional theory (DFT) based on quantum chemistry was used to solve the Schrodinger equation of the multi-electron system. Density functional theory (DFT) not only simplifies the Schrodinger equation of multi-particle system by using the Born–Oppenheimer approximation [47] (the terms of electron and atom nucleus motions are treated separately) and the Hartree–Fock approximation [48] (mean-field approximation), it also takes the Coulomb interactions between electrons into account. All the particles in the multi-electron system are regarded as identical particles, and the electron density was used as the variable of the energy functional theory for the calculation of the ground-state energy of the system so as to describe the physical properties of the ground state of atoms, molecules, and solids, and the relationships between the electronic structure and energy of the system. As a result, Hohenberg and Kohn proposed the theory of inhomogeneous electron gas, namely the famous Hartree–Fock approximation [49], and the energy of the multi-particle system is the function of electron number density. To further determine the exchange correlation of the energy functional and solve the energy functional, Kohn and Sham proposed the Kohn–Sham (KS) equation [50]. Compared with the Hartree–Fock approximation, the Kohn–Sham equation added two further terms of electron exchange interaction and electron correlation interactions. In the process of solving the electron density and energy using the KS equation, it is necessary to use the self-consistent field (SCF) method to make the calculated value converge below the set value. According to the electron probability density and energy after convergence, the ground-state and related properties of the system are deduced [51]. However, the Kohn–Sham equation only involved the electron probability density and kinetic-energy functional in the electron energy term, while further considerations of the potential energy term between electrons were missing. Therefore, it is necessary to further deal with the cross-linking energy between electrons. Currently, the commonly used approximation methods included local density approximation (LDA) [52], generalized gradient approximation (GGA) [53], and local spin density approximation (LSDA) [54]. Compared with LDA, GGA added the density gradient term of electron density between adjacent elements on the basis of LDA, which overcame the exchange-correlation energy of the non-uniform electron system. LDA is more suitable for calculating the metal system; therefore, GGA was selected for approximate calculation in this study. At present, the simulation calculation based on density functional theory has been widely used in biology [55], materials [56], minerals [57–59], and other fields.

Cadmium and other divalent ions are transported through the xylem and phloem in the form of free ions or organic complexes. Therefore, we used both organic acid complex cadmium [60] and free ions to simulate the biological toxicity of cadmium. In this work, both experiments and simulation calculations were used. Firstly, we verified the absorption of cadmium by the selected wetland plants through experiments and then calculated the cadmium enrichment coefficient, rhizome transport coefficient, and stem leaf transport coefficient of the plant to indicate the difference in absorption transport between plants. Secondly, the competitive absorption of cadmium, calcium, and iron on organic acids was then calculated by DFT to reveal the competitive advantage of cadmium. The biological

toxicity of cadmium was simulated according to the differential charge density and density of states (DOS) of different subcellular structures.

2. Materials and Methods

2.1. Data Acquisition

Five kinds of plants, namely, *Zephyranthes candida*, *Cynodon dactylon*, *Arundo donax*, *Phragmites communis*, and *Pontederia cordata*, were collected from a constructed wetland park in the upper reaches of the Yangtze River. According to the ecological characteristics of plants, the plants were cut into three parts of root, stem, and leaf. All samples were ground to powder (up to a mesh size of 100). The sample powder was divided into two parts. One part of the powder was directly observed by scanning electron microscopy (SEM, TM4000, Hitachi, Tokyo, Japan), and the distribution of cadmium in plants was analyzed by energy dispersive spectroscopy (EDS, TM4000, Hitachi, Tokyo, Japan) to judge the presence of cadmium in the plants directly. The other part of the sample powder was digested by nitric acid hydrogen peroxide to get a clear solution, and the specific content of cadmium in different parts of the samples was determined by inductively coupled plasma atomic emission spectrometry (ICP-OES, ICAP6500, Thermo Fisher, Waltham, MA, USA).

In order to quantify the absorption capacity of different plants for cadmium from the environment and transport cadmium within the plant body, the biological concentration function (BCF) and transport function (TF) were calculated by the following formula:

$$\text{BCF} = \text{total cadmium in plant} / \text{environmental cadmium content}$$

$$\text{TF1} = \text{stem cadmium content} / \text{root cadmium content}$$

$$\text{T2} = \text{CD content in leaves} / \text{CD content in stems}$$

where:

TF1 = transport coefficient of rhizome;

T2 = stem leaf transport coefficient.

2.2. Calculation Details

The calculation of quantum chemistry based on density functional theory was done using the Material Studio 7.0 software (Accelrys Software Inc., San Diego, California, USA). Molecular models of some common root metabolites, including citric acid, oxalic acid, tartaric acid, malic acid, succinic acid, and fumaric acid (as shown in Figure 1) [61,62], were established for the five experimental plants. The molecular models were established based on the main substances in the different subcellular structures. For example, chlorophyll A and chlorophyll B represent the chloroplast environment, while glucose and pyruvate represent the mitochondrial environment. The structure optimization and properties calculation of all the models was performed by means of quantum mechanical calculations based on DFT using the GGA (generalized gradient approximation) and PBE (Perdew–Burke–Ernzerhof) exchange–correlation functional [57–59]. The CASTEP was used for structure optimization and property calculations. The highly accurate full-potential projector-augmented-wave (PAW) method with ultrasoft pseudopotentials was used to describe the electron–ion interactions in the valence-band region. Brillouin-zone integrations were calculated with a gamma-centered $3 \times 3 \times 3$ Monkhorst-Pack k-point mesh. The convergence criteria for the energy, maximum force, maximum displacement, and SCF tolerance were set as 1.0×10^{-5} eV/atom, 0.01 eV/Å, 1.0×10^{-4} Å, and 1.0×10^{-4} eV/atom, respectively.

Figure 1. (A) oxalic acid, (B) citric acid, (C) malic acid, (D) tartaric acid, (E) pyruvic acid, (F) fumaric acid, (G) succinic acid, (H) glucose, (I) chlorophyll A, and (J) chlorophyll B.

3. Results and Discussion

3.1. Competitive Absorption of Cd, Ca, Zn and Fe on Root Exudates

The six kinds of organic acids secreted by roots, metal chloride (Cd, Ca, and Fe) in soil environment, and the configuration energy of corresponding complexes were calculated by CASTEP, as shown in Table 1. It should be noted that the calculated final energy is not of practical significance but only represents the value of the optimized configuration. Therefore, it is necessary to calculate the reaction energy barrier through the final energy of each molecular configuration (i.e., the amount of energy change in the reaction process) in order to measure the difficulty of different reactions. The formula is as follows:

$$E_b = E_c - (E_o + E_m)$$

where E_b is the reaction barrier, E_c is the final energy of organometallic complexes, E_m is the final energy of metal salt, and E_o is the final energy of organic acids.

Table 1. Energy of organic compounds and organometallic complexes.

Metal Form	E_m (eV)	Organic Acid	E_o (eV)	Complex Compound	E_c (eV)	E_b (eV)	Absorption Sequence
CdCl ₂	−2101.78	Oxalate	−2086.82	Cd	−3336.65	851.95	Fe > Ca > Cd
				Ca	−3058.06	850.5	
				Fe	−2916.99	849.3	
CaCl ₂	−1821.74	Citric acid	−4112.46	Cd	−5360.01	854.23	Ca > Cd > Fe
				Ca	−5080.93	853.27	
				Fe	−4935.89	856.04	
FeCl ₂	−1679.47	Malic acid	−2897.50	Cd	−4144.49	854.79	Ca > Cd > Fe
				Ca	−3865.79	853.45	
				Fe	−3722.80	854.17	
		Tartaric acid	−3327.23	Cd	−4554.81	874.2	Fe > Cd > Ca
				Ca	−4274.29	874.68	
				Fe	−4147.74	858.96	
		Fumaric acid	−2423.98	Cd	−3670.01	855.75	Fe > Ca > Cd
				Ca	−3391.84	853.88	
				Fe	−3251.39	852.06	
		Succinic acid	−2457.20	Cd	−3704.20	854.78	Cd > Fe > Ca
				Ca	−3423.22	855.72	
				Fe	−3281.53	855.14	

When cadmium and plant essential elements, calcium and iron, coexist in the environment, the absorption of the three elements is relatively average (Table 1). It was found that Cd^{2+} only occupied the absorption sites of Ca^{2+} and Fe^{2+} on succinic acid, while the absorption advantage of Cd^{2+} on malic acid and citric acid was not obvious. On the contrary, the absorption of Fe^{2+} and Ca^{2+} on oxalic acid, tartaric acid, and fumaric acid was hardly affected by Cd^{2+} . The reaction energy barrier of calcium citrate is 1 eV lower than that of cadmium citrate; thus, calcium ion has a weak absorption advantage over cadmium. Similarly, for the absorption on malic acid, calcium malate had the lowest energy barrier, while the energy barrier for cadmium and iron absorption is similar. Thus, the latter two have no obvious absorption advantage. The reaction energy barrier of ferric oxalate is about 3 eV lower than that of cadmium oxalate, indicating that free ferrous ions have a greater absorption advantage over cadmium element. It is worth noting that the energy barrier of Fe^{2+} absorption on tartaric acid is about 20 eV lower than that of cadmium and calcium (Table 1). According to the bond-valence theory, calcium ($3s^23p^6$) and cadmium ($4d^{10}5s^2$) are in a stable energy state, while iron ($3d^64s^2$) has four single-spin electrons in the d orbit of the sub-level, which is in an unstable energy state. The two hydroxyl groups in the tartaric acid molecule could more effectively excite the outer electrons of iron than the stable outer electrons of calcium and cadmium.

This can also explain why the energy barrier difference is quite small for the absorption of three kinds of ions on other organic acids. As with oxalic acid, citric acid, and malic acid, only one hydroxyl group exists in the molecular structure, which is insufficient to excite the iron d-orbital. No hydroxyl groups exist in fumaric acid and succinic acid: the C=C double bond in these two acids can only reduce the energy of the molecule itself, inhibiting the self-reaction activity, which leads to a higher reaction barrier. According to the structural formula of citric acid, the energy of citric acid is higher than that of tartaric acid ($4112.46 > 3327.23$). The reason for its higher energy is the presence of three carboxyl groups, indicating more unstable carboxyl hydroxyl groups. The capability to ionize protons indicated higher energy in the acid. Therefore, the excitation effect on the d-level single electron of iron may not be strong despite its higher energy. From the calculation results, most of the secreted acids can absorb cadmium and essential elements like calcium and iron simultaneously. However, organic acids secreted by plant roots notably have the possibility to decrease the absorption of essential elements due to cadmium absorption.

3.2. Cadmium Transport among Roots, Stems and Leaves

After entering the plant roots, cadmium will be transported to all parts of the plant. By analyzing the cadmium content in various parts of the plant, we can know whether the plant has defense measures against cadmium. In other words, the cadmium distribution and content within the plant body could indicate the ability of cadmium-tolerant plants to treat cadmium-contaminated soil or water bodies. It may also serve as a monitoring indicator for cadmium contamination of soil or water bodies. As shown in Figure 2, cadmium was present in all five plants. The absorption capacity for cadmium in the plants was in the order of *Z. candida* > *P. cordata* > *C. dactylon* = *A. donax* > *P. communis* (Table 2). The BCF of *P. communis* is less than 1, indicating that the plant is not an effective cadmium enrichment plant.

Plants with a strong stem are usually able to intercept cadmium. In other words, the stem could intercept cadmium in the gap between the cell wall and cytoplasm by mechanical blocking [63], which inhibits the transportation of cadmium in the plant body. It could be proven that the cadmium content in the stem of *C. dactylon* and *P. communis* was higher than that in the root and leaf. The diameters of the leaf and stem of the five wetland plants are presented in Table 3. The cadmium content in leaves of *C. dactylon* (0.008 ppm) and *P. communis* (0.006 ppm) was very low, which could be attributed to the strong interception by the stem. The stems of *C. dactylon* were quite thin. Since most of the plants are grown underground, the phloem tissues are very thick and the transpiration rate is weak; thus, the cadmium uptake of *C. dactylon* is large and the upward

transport is inhibited. Although *A. donax* has strong stems, cadmium is mainly concentrated in its leaves. This phenomenon could be ascribed to its super-large leaf. The strong transpiration by the leaves could drive the cadmium intercepted by the stems towards leaves again. Compared to *A. donax*, cadmium was evenly distributed in the stems and leaves of *P. cordata*. The leaf sizes of *P. cordata* are about half of *A. donax*, making the cadmium transportation rate within the plants similar to that of transpiration. Thus, the distribution of Cd in the stem and leaf was more uniform. Therefore, the transportation of cadmium in plants mainly depends on transpiration and mechanical interception of stem cell structure. Meanwhile, the tolerance of plants to cadmium can also be measured by the transport coefficient. As is well known, plants have evolved many new structures in the stem [47] to inhibit the diffusion of cadmium into fruits and seeds. Of all the wetland plants, the most cadmium was concentrated in the leaves of *Zephyranthes Candida* and *P. cordata* (Table 2). However, the stem–leaf transport coefficient of the latter was greater than 1, but its total amount of adsorbed cadmium was only half of the former. It can be concluded that the cadmium transport rate of *Zephyranthes Candida* is faster than that of the other three cadmium enrichment plants, while the cadmium tolerance of *Zephyranthes Candida* was poor. Although the TF2 of *A. donax* was larger than 1, its cadmium absorption amount was much lower, indicating the plant has evolved a relatively complete defense mechanism to avoid adsorbing a large amount of cadmium from the environment and accumulating cadmium in its stems. As a result, the fruits, leaves, and seeds are less polluted.

Figure 2. Distribution of cadmium in different plants by SEM-EDS (The pink dots represent the distribution of cadmium).

Table 2. Accumulated cadmium concentration of five wetland plants.

Plant	Root (PPM)	Stem (PPM)	Leaf (PPM)	Total Absorption (PPM)	Background Value (mg/kg)	BCF	TF1	TF2
<i>Zephyranthes candida</i>	0.013	0.036	0.024	0.073	1.602	1.62	2.77	0.67
<i>Cynodon dactylon</i>	0.016	0.017	0.008	0.041	1.602	2.00	1.06	0.47
<i>Arundo donax</i>	0.013	0.011	0.017	0.041	1.602	1.62	0.85	1.55
<i>Phragmites communis</i>	0.005	0.011	0.006	0.022	1.602	0.62	2.2	0.55
<i>Pontederia cordata</i>	0.01	0.016	0.021	0.047	1.602	1.25	1.6	1.31

Note: the background value is taken from Zeng et al. [11,12].

Table 3. Stem and leaf size of five plants.

Plants	Stem Diameter (CM)	Widest Part of Leaf (CM)
<i>Zephyranthes candida</i>	2.5	0.4
<i>Cynodon dactylon</i>	0.15	0.3
<i>Arundo donax</i>	3.5	5
<i>Phragmites communis</i>	4	2
<i>Pontederia cordata</i>	1	3

3.3. Reaction Mechanisms of Cadmium with Organic Compounds in the Subcellular Environment

When cadmium reaches leaves, fruits, and other organs in the plant, physiological toxicity in the subcellular structure would be present. In order to verify the physiological toxicity of cadmium, the changes of the main organic compounds in the subcellular structure after cadmium contamination in chloroplasts and mitochondrion were calculated. It is worth noting that the original organic compounds have no electrons of *d*-orbitals, and it is easy for cadmium to form *spd* orbital hybrids with the original organic compounds after complexation with cadmium. Combined with Figure 3, the density of states (DOS) of the cadmium pyruvate at ± 5 eV and cadmium gluconate at 5 eV changed significantly, indicating the formation of orbital hybridization. According to the differential charge density of Figure 3, the electron transport from the *d*-orbital of cadmium ion to the *s*- and *p*- orbitals of hydroxyl oxygen is the reason for the formation of the new complex. As shown on the left side of Figure 3, once complexed with pyruvate and glucose, as an electron donor cadmium provided 0.05 eV and 0.01 eV charge. The charge was transported to hydroxyl oxygen. As shown on the right side of Figure 3, the density of states of pyruvate and glucose after cadmium complexation shift to the left side, indicating that the properties of the complex are relatively stable. For cadmium pyruvate, the maximum energy of the *p*-orbital electron is increased from 6 eV to 8–10 eV, which indicates that cadmium pyruvate has a higher reactivity. However, the highest energies of *s*- and *p*- orbitals were respectively excited from 7 eV and 9 eV to 10 eV. The overall reactivity of the compound was enhanced and changed significantly. Using calculations, it has been confirmed that cadmium ions can contaminate pyruvate and glucose in the mitochondria by orbital hybridization. The pyruvate and glucose contaminated by cadmium will continue to participate in the metabolic process of cells, but the subsequent physiological process will be affected due to the change of electron energy distribution (density of states). Some research found that some plants have alternative respiration abilities to ensure normal respiration [64]. If the plants did not avoid using the contaminated glucose and the contaminated pyruvate, the glucose would flow to extracellular areas [65] and have an inhibition of growth leading to some morphology change, such as leaf area shrinkage and leaf chlorosis. However, most plants do not have alternative respiration abilities, thus the common respiratory process lesions are consistent with the calculation results. Meanwhile, the 30% electron activity enhancement may also explain the results of a previous study, that is, Cd could transport electrons to the electron donor, therefore meaning that the electron acceptor, some respiratory enzyme, cannot obtain electrons [44]. Furthermore, research also observed some important enzymes have a range of activity decline of 20–80% under a continued high concentration of Cd stress [66].

Mg²⁺ in the center of chlorophyll A and chlorophyll B molecular structure is prone to replacement by a copper substitution reaction, which could change the properties of chlorophyll and affect the normal photosynthesis of plants. As shown in Figure 4, after Mg²⁺ replacement with Cd²⁺, the differential charge density indicates that Cd²⁺ transports 0.01 eV charge to the surrounding four N atoms. Unlike cadmium pyruvate and cadmium glucose after cadmium doping, the PDOS suggest that there is no *spd* orbital hybridization since the energy peak and shape of *s*- and *p*- orbitals do not change significantly. When Mg²⁺ is replaced by Cd²⁺, the *s*-orbital electrons of chlorophyll are excited, and the peak energy of *s*-orbital at −40 eV disappears. According to the energy-band theory, the *s*-orbital electrons of chlorophyll contaminated by cadmium could become more concentrated, making some cadmium appear in the deeper *s*-orbital electron valence band and excite the

higher-energy valence band. However, the electron energy of the rest of the *s*- and *p*- orbitals did not show distinct shift and peak changes, which indicated that Mg^{2+} determined the *s*-orbital at 40 eV of chlorophyll, and that the structure of chlorophyll may become much more unstable due to the substitution of Cd^{2+} . The essence of chemical reactions is the interactions between electrons. It is possible that due to the lack of electron activity at -40 eV, cadmium-doped chlorophyll may not be able to participate in some subsequent physiological processes. Previous research found a spatial leaf heterogeneity of decreased PSII (a photosynthesis pathway) photochemistry in the early stage of Cd containment which later completely recovered [67]. We thought the early abnormal photosynthesis resulted from the Cd substitution. With respect to the reported study, the *Noccaea caerulea* has a Cd defense ability so the subsequent photosynthesis turned to normal. For the five plants in our experiment, whether the Cd defense ability existed, the influence on photosynthesis is certain. Another example is that a strong reduction in the maximum photochemical efficiency of PSII was observed [68]. It perhaps resulted from the fact that the chlorophyll-cadmium compounds are unstable and the valence electrons disappear at -40 eV.

Figure 3. Reaction mechanisms of cadmium with mitochondrial components.

Figure 4. Reaction mechanism between cadmium and chloroplast components.

4. Conclusions

Considering the increasing cadmium pollution in water and soil in Southwest China, five wetland plants were collected from the constructed wetland in the upper reaches of the Yangtze River, namely the Tuojiang River. Various experiments and simulations were performed to reveal cadmium absorption from the environment by plants, the efficiency of cadmium accumulation and transport in plants, as well as the effects of cadmium on physiological processes in the subcellular structure. According to the experimental results, the order of cadmium absorption is *Z. candida* > *P. cordata* > *C. dactylon* = *A. donax* > *P. communis*. There were obvious differences in the absorption capacity among the five wetland plants, particularly between *P. communis* and the other four plants: the absorption capacity of *P. communis* for cadmium was lower compared to the rest of the plants. The transport coefficient of the stems and leaves of *A. donax* and *P. cordata* was more than 1, suggesting poor tolerance to cadmium. Furthermore, cadmium was easily enriched in the leaves, fruits, and seeds of *P. cordata*.

By simulating the reaction energy barrier of root exudates with Cd, Ca, and Fe, it was found that there was no obvious absorption advantage of the three metals; that is, Cd did not inhibit the entry of Ca and Fe into plants. Meanwhile, in the subcellular structure, it was found that Cd^{2+} could hybridize with the main materials of mitochondria, glucose, and pyruvate by providing *d*-orbital electrons. The peak energy of *s*- and *p*- orbitals increased by 30%, the organic molecules became more unstable, and the reactivity increased. In the chloroplast, the substitution of Mg^{2+} by Cd^{2+} via a copper replacement reaction resulted in valence-electron vacancy at -40 eV. As a result, the whole electron energy of chlorophyll became more concentrated, which reduced the stability of the molecular structure of chlorophyll. Thus, Cd^{2+} plays an important role in the subcellular structure since it could

react with key organic compounds for the subsequent physiological process. However, from a quantum chemistry perspective, the underlying mechanisms are still unclear.

Nevertheless, the combination of experiment and DFT calculation methods used in this paper can provide data and method references for follow-up studies on pollutant absorption by plants, pollutant transport and reaction at the molecular level, as well as provide perspectives for related research.

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