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Mechanism of Cd(II) adsorption by macrofungus *Pleurotus platypus*

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Abstract

The mechanism of Cd(II) uptake by the dead biomass of macrofungus *Pleurotus platypus* was investigated using different chemical and instrumental techniques. Sequential removal of cell wall components of the biosorbent revealed that structural polysaccharides play a predominant role in the biosorption of Cd(II). The adsorption kinetics fitted well with the pseudo second-order model suggested that the adsorption of Cd(II) on *P. platypus* involved a chemisorption process. Transmission electron microscopy of the cadmium exposed biomass confirmed the deposition of the metal mainly in the cell wall. Fourier transform infrared spectroscopic analysis of the metal loaded biosorbent confirmed the participation of –OH, –NH and C–O–C groups in the uptake of Cd(II). Energy dispersive X-ray analysis of the biosorbent before and after metal uptake revealed that the main mechanism of adsorption was ion-exchange. The effectiveness of $CaCl_2$ in the desorption of cadmium perhaps suggested the exchange of Ca^{2+} with Cd(II).

Key words: biosorption; mechanism; ion-exchange; *Pleurotus platypus*; macrofungus; cadmium

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Introduction

Cadmium receives wide attention by environmentalists as one of the most toxic heavy metals. The increasing presence of cadmium in the environment is mainly due to its use in electroplating, paint pigments, plastics, alloy preparation, mining, ceramics and silver-cadmium batteries (Volesky, 1990; Wase and Forster, 1997). Cadmium toxicity may be observed by a variety of syndromes and effects including renal dysfunction, hypertension, hepatic injury, lung damage and teratogenic effects (Yu et al., 1999; Kaewsarn and Yu, 2001; Lodeiro et al., 2006). Because of the toxicity and bioaccumulation, Cd(II) is considered as a priority pollutant by the US Environmental Protection Agency. The permissible limit for Cd(II) as described by World Health Organization is 0.01 mg/L. The usual methods for removal of heavy metal ions from aqueous solutions are chemical precipitation, ion exchange, solvent extraction, phytoextraction, ultrafiltration, reverse osmosis, electrodialysis, and adsorption (Patterson, 1985; Bhattacharya et al., 2006). However, technical or economic factors limit the feasibility of such processes. Most of these methods suffer from some drawbacks, such as high capital and operational cost or the disposal of the residual metal sludge, and are not suitable for small-scale industries (Kobya et al., 2005).

Biosorption which utilizes biological materials as adsorbents is an emerging technology for the removal of heavy metals from industrial wastewater. The main advantages of this technique are the reusability of biomaterial, low operating cost, improved selectivity for specific metals of interest, removal of heavy metals from effluent irrespective of toxicity, short operation time, and no production of secondary compounds which might be toxic (Mungasavalli et al., 2007). It employs a wide variety of biomasses, such as fungi, algae and bacteria, for removal of metal ions (Sag and Kutsal, 2000; Gupta et al., 2001; Nourbakhsh, 2002).

Although several proprietary biosorption processes such as AlgaSORB™ (Brierley et al., 1986) and AMT-Bioclaim™ (Darnall, 1991) have been developed and commercialized, a lack of understanding of the mechanism underlying the metal-sorption process has hindered adequate assessment of process performance and thus the expected widespread application of biosorption. Encouraging results from our previous study (Vimala and Das, 2009) has stimulated interest in understanding the mechanism of Cd(II) uptake by the macrofungus *Pleurotus platypus*. As far as the authors are aware, there are scanty reports in the literature on the mechanism of Cd(II) biosorption by macrofungi. Therefore, the real challenge for the field of biosorption will be to identify the actual mechanism of metal uptake by the biosorbents. Elucidation of metal uptake mechanism may provide a useful basis for manipulation and improvement of the biosorbent selectivity for the desired metal (Kuyucak and Volesky, 1989). The objective

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of the present study is to investigate the mechanism of Cd(II) biosorption by *P. platypus* using different analytical approaches like Fourier transform infrared spectroscopy (FT-IR), energy dispersive X-ray (EDAX), Transmission electron microscopy (TEM) and experimental approaches like kinetic study and desorption.

1 Materials and methods

1.1 Materials and solutions

The fruit bodies of *P. platypus* were obtained from the mushroom farm of Krishi Vigyan Kendra (Tamil Nadu Agricultural University), Virinjipuram, Vellore District, Tamil Nadu, India. The samples were washed and dried for 48 hr in an oven at 40°C, and then pulverized in a hand grinder to yield powdered particles. Standard stock solution of Cd(II) ions (1000 ± 2) mg/L prepared from its nitrate salt (sd-fine Chem. Ltd., India) was used to prepare appropriate concentrations of the metal for the sorption studies. pH of the working solutions was adjusted to 6.0 using 0.1 mol/L NaOH and 0.1 mol/L HCl. Cadmium analysis was done using atomic absorption spectrophotometer (Varian AA 240, Australia) under the following conditions: wavelength 228.8 nm; slit 0.5 nm; type of flame air-acetylene.

1.2 Sequential removal of cell wall components of the biosorbent

A sequential removal technique was employed using raw biosorbent (BR) to remove different components of fungal cell wall to assist in the elucidation of the role of individual cellular components in the metal sequestering process. The scheme for sequential removal is presented in Fig. 1.

Lipid extraction from BR was done using methanol-chloroform mixture following the method of Nakajima et al. (1981) with minor modifications. The first derivative (BL) thus obtained was treated with 2 mol/L NaOH for the removal of protein. Thereby, the second derivative (BP) devoid of lipid and protein was subjected to hot alkali treatment (40% NaOH) at 120°C for the removal of structural polysaccharides following the method of Muzzareli et al. (1980) with minor modifications. The third derivative obtained designated as (BSP) was devoid of lipid, protein and polysaccharides. BR along with other three derivatives (BL, BP, and BSP) were used in metal uptake studies.

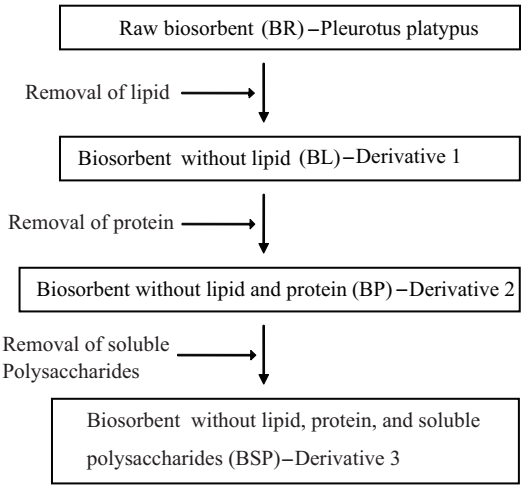

Fig. 1 Scheme for sequential removal of cell wall components of *P. platypus*.

1.3 Sorption studies

Biosorption experiments were optimized at the desired pH value, contact time and biomass dosage level in our previous study (Vimala and Das, 2009). Batch experiments were conducted in 250 mL conical flasks with a working solution of volume 100 mL adjusted to pH 6.0 and at temperature (28 ± 1)°C. The 0.1 g of BR and different derivatives (BL, BP and BSP) were added separately to the Cd(II) ion solutions (10–100 mg/L) and agitated in a rotary shaker at 125 r/min. After equilibrium the metal solutions were filtered and the residual metal concentration in the filtrate was analyzed.

Rate of metal sorption by *P. platypus* was determined by analyzing residual metal ions in the supernatant after contact periods of 5, 10, 15, 20, 25, 30, 45, 60 min, 2, 3, 4, 5 and 6 hr. A blank containing 100 mL of cadmium ion solution without any adsorbent was shaken simultaneously to determine any adsorption of cadmium onto the walls of the conical flasks. A control, with 100 mL of deionized water (no metal ion added) and the biosorbent was also shaken to determine any leaching of cadmium from mushrooms.

1.4 Desorption studies

Cadmium loaded raw biosorbent was dried and shaken with 100 mL of 0.1 mol/L $CaCl_2$ as desorbing agent at 125 r/min on an orbital shaker for 3 hr at (28 ± 1)°C. The metal loaded biosorbent was separated by filtration and the filtrate was analyzed for metal ions desorbed.

1.5 Transmission electron microscopy (TEM)

Raw biosorbent used for TEM analysis was previously contacted with Cd(II) solution and fixed by submerging them in 3% (*W*/*V*) glutaraldehyde and washed with buffer. Then it was fixed by 1% osmium tetroxide and washed in buffer. The samples were washed repeatedly with 0.1 mol/L phosphate buffer and dehydrated in a graded alcohol (50%–100%) and cleared by propylene oxide. Infiltration was carried out by propylene oxide and epoxy resin and embedded in siligonised rubber mould with epoxy resin. The resin infiltration steps were carried out at 20°C and eventually the samples were transferred into molds for polymerization at 60°C for 48 hr. Sections were obtained using a Leica ultracut UCT ultramicrotome and stained by Toluidine Blue. Sections were examined with a Philips 201C (Philips, the Netherland) TEM.

1.6 Fourier transform infrared spectral analysis

Infrared spectra were recorded on an Avatar 330 model (Thermo Nicolet Co., USA) FT-IR spectrometer. For IR studies 5 mg of biosorbent was encapsulated in 400 mg of KBr. Translucent discs were obtained by pressing the

ground material with the aid of a bench press. Each experiment was repeated at least twice.

1.7 Energy Dispersive X-Ray (EDAX) analysis

EDAX analysis were conducted using Noran System Six model Energy Dispersive X-Ray Microanalysis System (Thermo Electron Corporation, Japan) attached to the SEM. Accelerating voltage was kept constant at 15 kV, to facilitate the emission of secondary X-rays.

2 Results and discussion

2.1 Elucidation of the role of different cell wall components in biosorption of cadmium

The Cd(II) uptake capacities of the different biosorbents (BR, BL, BP and BSP) were determined by fitting the experimental data using Langmuir isotherms models (Fig. 2). BL failed to show any significant change in metal uptake capacity (32.73 mg/g) compared BR (33.67 mg/g) which suggested that the role of lipids is not significant in Cd(II) biosorption. Alkali treatment with 2 mol/L NaOH to remove proteins showed an increase in metal uptake (40.65 mg/g). This increase might be due to the unmasking of active binding sites involved in biosorption of Cd(II). Thus it was evident that both protein and lipid are not involved in uptake of cadmium. The metal uptake after the removal of lipid and protein may be due to the involvement of polysaccharides. Finally the hot alkali treatment removed the alkali soluble polysaccharides like mannoproteins and some α- and β-(1,3)-D-glucan leaving behind the alkali insoluble polymers including β-(1,3)-D-glucan, β-(1,6)-D-glucan, chitin, chitosan and cellulose (Liu, 2003). Thus the removal of alkali soluble fraction of polysaccharides by hot alkali treatment showed a decrease in metal uptake. The residue left after the removal of lipid, protein and alkali soluble polymers still showing a cadmium uptake capacity of 28 mg/g proved that not only soluble but insoluble polysaccharides also play a fairly important role in biosorption of Cd(II).

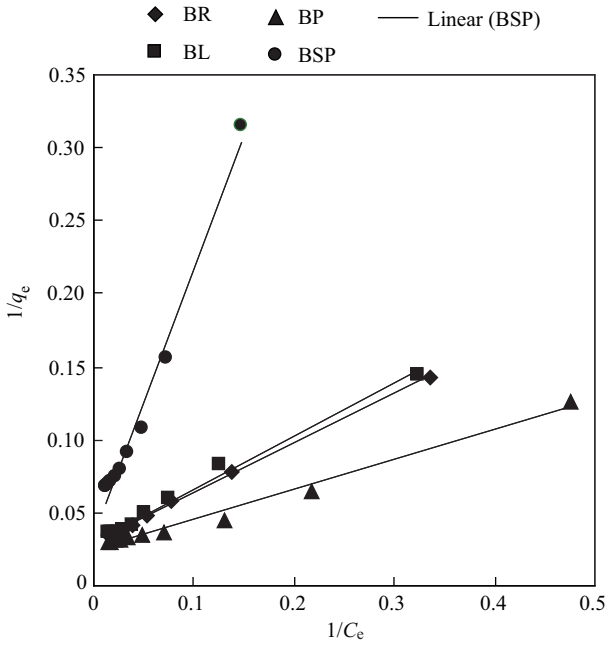

Fig. 2 Langmuir isotherm model for Cd(II) biosorption. BR: raw biosorbent; BL: biosorbent without lipid; BP: biosorbent without lipid and protein; BSP: biosorbent without lipid, protein and soluble polysaccharides. Conditions: pH 6.0, biomass dosage 1 g/L; contact time 6 hr; temperature (28 ± 1)°C.

2.2 Desorption of cadmium with $CaCl_2$

If the biosorption process is to be used as an alternative in wastewater treatment, the regeneration of the biosorbent may be crucially important to keeping the processing cost down and to opening the possibility of recovering the metals extracted from the liquid phase. Desorption can, in many cases, also be interpreted in terms of ion exchange (Volesky, 2003). If ion exchange is the adsorption process, then eluting and regenerating the metal loaded biosorbent using a low cost and less polluting ion (e.g., Ca) other than proton at higher concentration is a feasible process. Thus desorption helps in regenerating the biosorbent and also to determine the mechanism involved in biosorption of the metal. In the present study about 72% of the metal was desorbed when $CaCl_2$ (0.1 mol/L) was used as a desorbing solution, suggesting that the sorbed cadmium ions on the biosorbent were exchanged for calcium ions in the desorbing solution. Thus ion exchange could play a significant role in the biosorption of cadmium by *P. platypus.*

2.3 Biosorption kinetics

In order to clarify the biosorption kinetics of Cd(II) ions onto *P. platypus* two pseudo first-order and pseudo second-order model were applied to the experimental data.

The linear form of the pseudo first-order rate equation (Lagergren, 1898) is given as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

where, q_e (mg/g) and q_t (mg/g) are the amounts of the metal ions biosorbed at equilibrium and time t (min), respectively, and k_1 (min^{-1}) is the rate constant of the equation. k_1 was determined experimentally by plotting of $\ln(q_e - q_t)$ versus t. The experimental values ($q_{e,exp}$ were not in good agreement with the theoretical values calculated ($q_{e,cal}$). Therefore, the pseudo first-order model is not suitable for modeling the biosorption of Cd(II) ions onto *P. platypus*.

Experimental data were also tested by the pseudo second-order kinetic model which is given in the following form (Ho and Mckay, 1999):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

where, k_2 (g/(mg·min)) is the rate constant of the pseudo second-order equation, q_t (mg/g) and q_e the amount of metal ions sorbed at any time t and at equilibrium The linear plot of t/q_t versus t for the pseudo second-order model for the biosorption of Cd(II) ions onto *P. platypus* is shown in Fig. 3. The rate constants values are given in Table 1. It is clear from these results that although the R^2 values are high in the both cases, the theoretical $q_{e,cal}$

values in case of pseudo second-order model were closer to the experimental $q_{e,exp}$ values (Table 1). These observations show that metal sorption by *P. platypus* followed the second-order reaction, which suggests that the process controlling the rate may be a chemical sorption involving valence forces through sharing or exchanging of electrons between sorbent and sorbate (Ho and Mckay, 1998).

2.4 TEM studies

TEM studies of the biosorbent *P. platypus* before and after cadmium adsorption were conducted to understand the location of the migrated metal after adsorption. The micrographs of the biosorbent before and after cadmium adsorption are given in Fig. 4a and b, respectively. Significant changes in the cell wall of biosorbent were observed after cadmium adsorption. Deposition of metal in the form of continuous band was noted on the outer surface of the cell wall in case of cadmium adsorbed cell (Fig. 4b) which indicated that metal ions did not penetrate the cellular membrane and the biosorption process is totally metabolism independent.

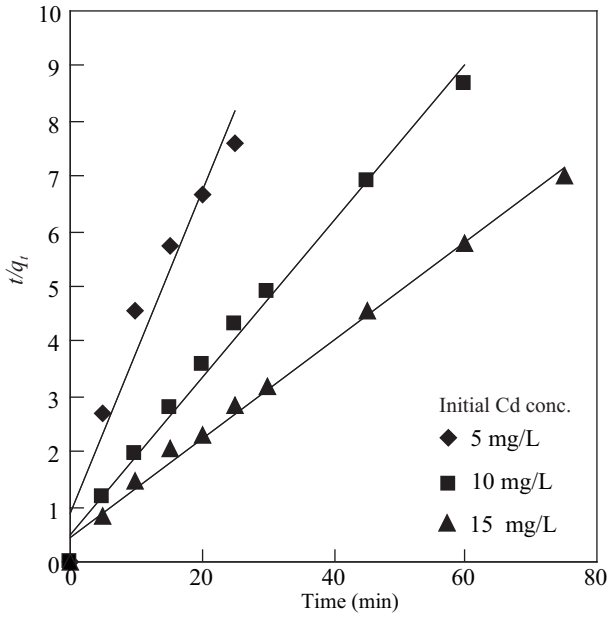

Fig. 3 Pseudo second-order kinetic model of Cd(II) biosorption onto *P. Platypus*. pH: 6.0; biomass dosage: 1 g/L; contact time: 5–360 min.

2.5 FT-IR spectroscopy

Infrared spectra can yield valuable information regarding the chemical groups possessed by the biosorbents. In the present study, the main effective binding sites have been identified by FT-IR in the spectral comparison of the raw and cadmium adsorbed biosorbent. As shown in Fig. 5 line a, the spectra display several vibrational bands indicating the complex nature of the material examined. The broad and strong bands at 3359 cm^{-1} were due to bounded hydroxyl (–OH) or amine (–NH) groups of the biomass. The peaks observed at 2922 cm^{-1} can be assigned to the –CH group of the biomass. The peaks at 1651 cm^{-1} were attributed to stretching vibration of carboxyl group (–C=O). Peak position at 1409 cm^{-1} indicates –NH stretching. The absorption peaks at 1157 cm^{-1} for P=O depict the presence of phosphate groups. The moderately strong absorption band at 1043 cm^{-1} could be assigned to the C–O–C stretching of sugars.

In the case of cadmium loaded biosorbent the stretching vibration of –OH group was shifted from 3359 to 3399 cm^{-1} (Fig. 5 line b). These results revealed that chemical interactions between the metal ions and the hydroxyl

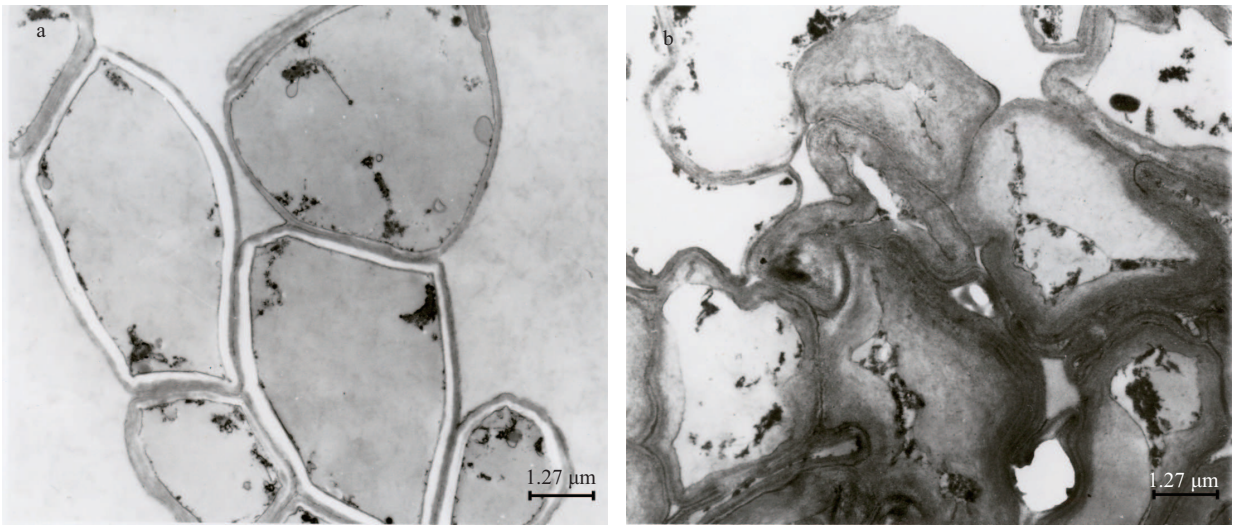

Fig. 4 Transmission electron micrograph of biosorbent *P. platypus* before (a) and after (b) adsorption of Cd(II).

Table 1 Kinetic model rate constants for Cd(II) adsorption on *P. platypus*

Initial Cd(II) (g/L)	$q_{e,exp}$ (mg/g)	First-order kinetic model			Second-order kinetic model		
		k_1 (min^{-1})	$q_{e,cal}$ (mg/g)	R^2	k_2 (g/(mg·min))	$q_{e,cal}$ (mg/g)	R^2
5	3.52	0.105	2.78	0.940	0.164	3.43	0.948
10	6.93	0.045	3.13	0.987	0.140	7.04	0.991
15	10.72	0.048	6.41	0.990	0.097	11.18	0.991

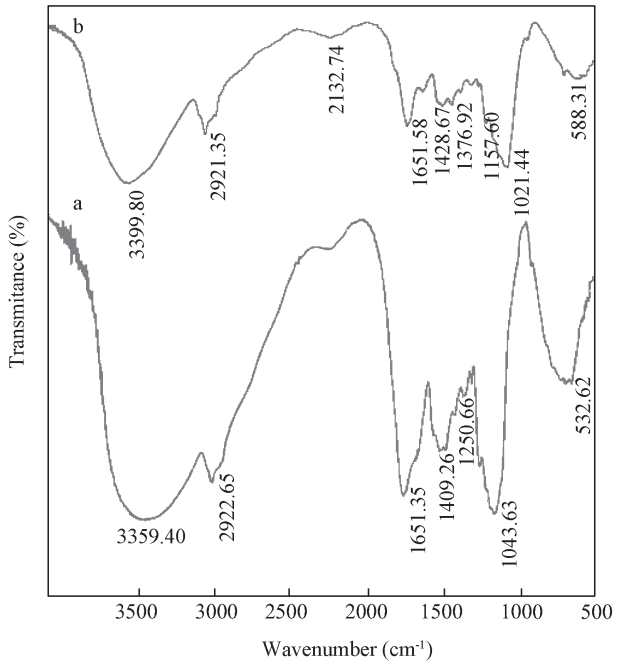

Fig. 5 FT-IR spectra of biosorbent *P. platypus* before (a) and after (b) Cd(II) adsorption.

groups occurred on the biomass surface. A shift in the band from 1409 to 1376 cm^{-1} and also from 1043 to 1021 cm^{-1} was noticed. The results suggest the participation of –OH, –NH and –C–O–C groups in the binding of cadmium. Similar results were reported for the biosorption of cadmium and copper onto the fungal biomass *Botrytis cinerea* (Akar and Tunali, 2005), cadmium biosorption by *Lentinus edodes* (Chen et al., 2008) and arsenic biosorption by *Inonotus hispidus* (Sari and Tuzen, 2008).

2.6 EDAX analysis of biosorbent

EDAX analysis provides elemental information through analysis of X-ray emissions caused by a high energy electron beam. EDAX technique can beneficially be employed to understand the elemental composition of the biosorbent. In the present study, X-ray dispersion analysis of the raw as well as cadmium adsorbed biosorbent *P. platypus* was conducted. The EDAX spectrum of biosorbent before Cd(II) adsorption indicated the presence of Na, K, Ca, Mg, Mn, Cl, and O as natural species on the biosorbent (Fig. 6a). These signals are due to X-ray emissions from the polysaccharides and proteins present on the cell wall of the biomass. Whereas, after Cd(II) adsorption, elements like calcium and magnesium signals are no longer predominant and cadmium signals are now distinctive (Fig. 6b). This indicates the possibility of cadmium replacing calcium and magnesium from the cellular material. The presence of these elements viz. calcium and magnesium could influence the adsorption mechanism which is thought to be ionic exchange interactions. Thus the present results could be indicative of the presence of ion exchange mechanism between these elements and Cd(II) on the surface of the biosorbent.

Apart from the basic building blocks, calcium is the most abundant constituent of biological systems. Calcium is found principally in extracellular locations, its main function being the stabilization of structural components of cells, i.e., extracellular proteins, cell membranes and cell walls (Williams, 1981). It is therefore likely that cellular components responsible for biosorption had calcium in their molecular structure.

3 Conclusions

All results obtained from both chemical and instrumental analysis support the hypothesis of ion exchange mechanism being involved in the binding of cadmium with the biosorbent *P. platypus*. The kinetic data signified that the biosorption of Cd(II) ions onto *P. platypus* followed well the pseudo second-order kinetic model supporting the concept of chemical ion-exchange. The chemical analysis reveals that polysaccharides play an important role in the biosorption of cadmium. The current results show that biosorption of metal ions on the biosorbent *P. platypus* released calcium and magnesium ions suggesting that the metal binding mechanisms of the biosorbent are similar to binding of heavy metals by ion exchange resins which are commonly used in water and wastewater treatment. EDAX analysis of cadmium-laden biosorbent confirmed the presence of cadmium on the biomass without showing any peak for calcium and magnesium. Undetected calcium and magnesium ions with EDAX would be the indication

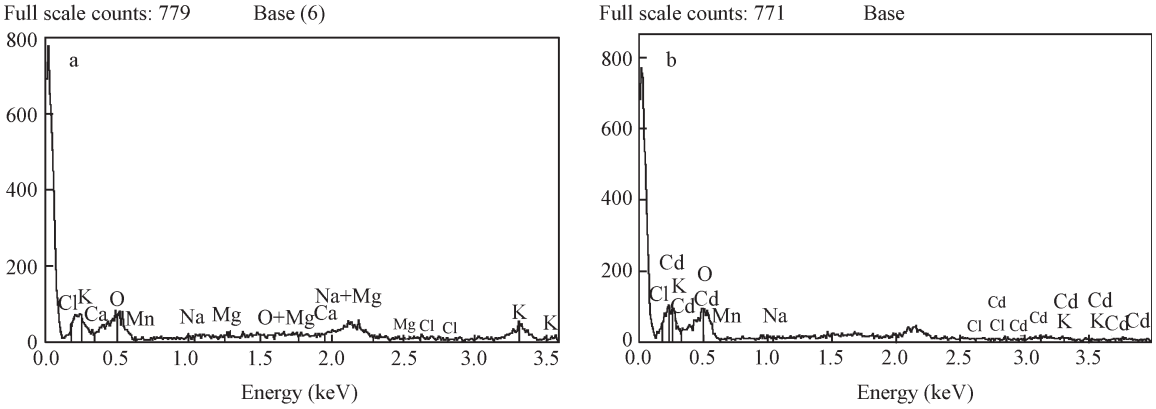

Fig. 6 EDAX Spectrum of biosorbent *P. platypus* before (a) and after (b) adsorption of Cd(II).

of the peaks that were apparently exchanged for the cadmium ions.

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