

Fixation of Heavy Metals onto Lignocellulosic Sorbent Prepared from Paddy Straw

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ABSTRACT: The sorption behavior of biosorbent prepared from paddy straw with nine different heavy metals has been studied. The binding mechanisms involving adsorption and the cation-exchange process have also been investigated. Characterization of biosorbent through a scanning electron microscope revealed no major surface deformity resulting from the chemical treatment. X-ray photo electron spectroscopy was also used to determine the presence of exchangeable cations in the sorbent and the speciation of bound chromium, cadmium, and mercury. The maximum sorption capacity (millimoles/gram) obtained from the Langmuir model for Pb^{2+} , Cd^{2+} , Hg^{2+} , Co^{2+} , Ni^{2+} , Mn^{2+} , Zn^{2+} , and Cu^{2+} were 0.286, 0.147, 0.226, 0.181, 0.196, 0.189, 0.219, and 0.248, respectively. Interpretation of Dahlquist (1978) and Scatchard (1949) was also used for the binding site heterogeneity. The unique ability of the biosorbent to bind nine different metals has been attributed to the presence of surface heterogeneity and Ca^{2+} ions, which attract and sequester metal ions. Biosorption results are useful for the development of low-cost biosorbent. *Water Environ. Res.*, **80**, 2165 (2008).

KEYWORDS: fixation, mechanism, heavy metals, paddy straw.

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Introduction

The major sources of heavy metal contamination of the environment are wastewaters produced in various industrial activities, such as mining, metallurgy, electroplating, electronics, metal finishing, leather tanning, chrome plating, batteries, phosphate fertilizers, pigments, stabilizers, alloys, chemical processing, and wood preservatives (Pandey et al., 1985; Richardson, 1978). It has been reported that more than 50 000 metal-contaminated sites in the United States need to be remediated (Ensley, 2000). The metals are potential hazards to aquatic, animal, and human life because of their toxicity and bioaccumulative and nonbiodegradable nature (Krishnani et al., 2003). Lead, cadmium, mercury, and chromium have been classified as priority pollutants by the U.S. Environmental Protection Agency (Washington, D.C.) (U.S. EPA), as a result of their major effect on the environment (Keith and Telliard, 1979; Volesky, 1994). Conventional methods, such as chemical

precipitation, are limited, as a result of technical constraints and their insufficiency to meet strict regulatory requirements (Cantrell et al., 1995; Meng and Letterman, 1996; Shokes and Moller, 1999). Reverse osmosis and ion exchange suffers from the high operational cost and cost of regeneration treatment (Benito and Ruiz, 2002; Ouki and Kavannagh, 1997; Rengaraj et al., 2001). Different types of unconventional biomaterials from agroindustries have shown levels of metal uptake high enough to warrant further research (Igwe and Abia, 2006; Krishnani and Ayyappan, 2006). To develop new processes for water treatment, various lignocellulosic agro-wastes, such as sugarcane bagasse (Krishnani et al., 2004), cellulose powder from wood pulp (Acemioglu and Alma, 2001), coconut fiber (Parimala et al., 2004), wheat bran (Bouanda et al., 2002; Dupont and Guillon, 2003; Ravat et al., 2000), sugar-beet pulp (Gerente et al., 2000; Reddad et al., 2002; 2003), and rice husk (Roy et al., 1993; Tarley et al., 2004; Wong et al., 2003) have been examined for their sorptive properties. However, technological and mechanistic aspects of heavy metals removal using biosorbents are scarce (Igwe and Abia, 2006). Paddy straw is an abundantly available byproduct of the paddy industry, whose production varies from 12 to 15 tons/ha, depending on the location and varieties. Previous reports on the use of paddy straw are limited only to chromium adsorption (Gao et al., 2007; Lal, 2002; Sekar and Giri, 2004) and the effect of dissolved organic matter derived from rice straw on heavy metals adsorption in soil and sludge (Cai et al., 2007; Chen and Chen, 2002). The aim of the present work is to study the sorption capacity of low-cost biosorbent prepared from partial delignification of paddy straw, for nine different metal ions (Pb^{2+} , Cd^{2+} , Hg^{2+} , Co^{2+} , Ni^{2+} , Mn^{2+} , Zn^{2+} , Cu^{2+} , and Cr^{6+}) in monometallic solution and compare their fixation onto the biosorbent as a function of pH and initial metal concentration. The role of cations present in the substrate on ion exchange or adsorption or both has been investigated.

Methodology

Biosorbent Preparation. Paddy straw (200 g) was mixed with 500 mL of 1.25% by weight sodium hydroxide and then autoclaved for 20 minutes, to remove the low-molecular-weight lignin compounds. This material was filtered and then washed with deionized water until the pH reached a constant value of 7 ± 0.1 . This fraction was then dried in an oven at 45°C until constant weight and then ground and dry sieved to 1 mm of particle size.

Characterization of Biosorbent. The lignocellulosic biosorbent from paddy straw was characterized using a scanning electron microscope (LEO 986, Carl Zeiss Inc., Thornwood, New York) with double-sided carbon tape.

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X-ray photo electron spectroscopy (XPS) was used to characterize the surface chemistry of the lignocellulosic substrate. Information was obtained on the elemental composition of the surface to a depth of approximately 0.1 to 1 nm. The XPS spectra of the biosorbent after exposure to metal ion solution were obtained on a PHI model 5400 axis Ultra Kratos Analytical instrument (Kratos Analytical, Manchester, United Kingdom). The X-ray source was run at 100 W, and the spectra were recorded at 15 kV. The analyzer chamber pressure was in the 1×10^{-7} to 1×10^{-10} Torr range. Binding energies were calibrated by assuming 284.6 eV for the C-C component of the C_{1s} line.

Batch Equilibrium Adsorption Study. Batch experiments were performed at $31 \pm 0.5^\circ\text{C}$ at $\text{pH } 6.5 \pm 0.1$. A prehydration of 1 hour for the biosorbent resulted in the stabilization of the solution pH. After the introduction of the initial concentrations of metal ions in the range 50 to 200 mg/L, the solution pH was either naturally buffered or adjusted with HNO_3 to constant pH 6.5. The flasks were agitated. After equilibration, the solution was filtered using a $0.45\text{-}\mu\text{m}$ filter, and the filtrate was used for the analysis of metals and calcium elements with an inductively coupled plasma (ICP) emission spectrometer (Varian Liberty- 200, Palo Alto, California).

To determine the reduction of Cr^{6+} , a batch experiment was performed at pH 2. The flask, with Cr^{6+} solution and the biosorbent, was agitated in an incubator. Samples were collected at suitable time intervals. The samples were filtered through a $0.45\text{-}\mu\text{m}$ filter. Filtered solutions were analyzed for hexavalent and total chromium. The diphenyl carbazide method (APHA et al., 1989) using a UV-visible spectrophotometer was used to detect Cr^{6+} . Total chromium was determined by the ICP method. The difference in concentration between total chromium and Cr^{6+} was taken as the concentration of trivalent chromium.

The mechanistic parameters associated with metal ion adsorption were obtained by fitting the results to the Langmuir model and following the interpretation of Dahlquist (1978) and Scatchard (1949). The Langmuir model enables us to estimate maximum fixation capacities and the stability of the metal-sorbent complexes. Interpretation of Dahlquist (1978) and Scatchard (1949) reveals binding site heterogeneity.

Effect of pH. To evaluate the effect of pH on the sorption capacity, metal solution at different pH values (2, 4, and 6.5) were allowed to equilibrate with the biosorbent in an incubator agitated at 150 rpm. After equilibration, the sample was filtered using a $0.45\text{-}\mu\text{m}$ filter, and the filtrate was analyzed for metals.

Leaching Study of Bound Metal Ions. To test leaching of bound metals from biosorbent, a batch experiment was conducted with aqueous solution of varying pH values (1.8 ± 0.2 , 4.2 ± 0.2 , and 6.3 ± 0.2) adjusted with HNO_3 , with the biosorbent loaded with metal ions at pH 6.5.

Results and Discussion

Characterization of the Substrate Using Scanning Electron Microscopy. Figures 1a and 1b show the scanning electron microscope (SEM) images of raw paddy straw, while the images of the sorbent prepared from the straw are shown in Figures 1c and 1d. These figures are shown at different magnification. The SEM images of the raw paddy straw and the sorbent show no major surface deformations, as a result of the chemical treatment, which has smoothed the surface by removing dust particles. These images also revealed high porosity and high surface area of paddy straw.

Biosorption of Heavy Metals onto Lignocellulosic Sorbent. Results of the equilibrium adsorption experiment for the initial

metal concentration of 200 mg/L and corresponding release of Ca^{2+} at $31 \pm 0.5^\circ\text{C}$ and $\text{pH } 6.5 \pm 0.1$ are given in Table 1. This indicates that metal sorption capacity of the partially delignified product from paddy straw in the present study is comparable or considerably greater than reported lignocellulosic substrates and other sorbents. The reported values of adsorption capacities for various metals on rice husk are 4 mg Cd/g and 45 mg Pb/g (Tarley et al., 2004) and 108 mg Pb/g and 29 mg Cu/g (Wong et al., 2003); for bagasse, 13.4 mg Cr^{6+} /g (Sharma and Forster, 1994); for sugar beet pulp, 10 mg Cr^{3+} /g (Reddad et al., 2003); for coconut husk fiber, 29 mg Cr^{6+} /g (Tan et al., 1994); for palm pressed fibers, 15 mg Cr^{6+} /g (Tan et al., 1994); for sugar beet pulp, 60 mg Pb/g, 30 mg Cu/g, and 12 mg Ni/g (Dupont and Guillon, 2003); for bagasse fly-ash, 1.4 mg Cd/g and 1.2 mg Ni/g (Gupta and Ali, 2004), Cr^{6+} 20, and Pb 30 (Gupta et al., 2003); for dead biomass from *Solanum elaeagnifolium*, Cd 18.94, Cr^{6+} 2.16, Pb 20.6, Zn 6.96, Cu 13.14, and Ni 6.5 mg/g (Baig et al., 1999); for wheat bran, Pb(II) 69 mg/g (Bulut and Baysal, 2006); and, for *Hemidesmum indicus*, Pb 93.6 mg/g (Chandra Sekhar et al., 2004).

It is evident, from Table 1, that the amount of Ca^{2+} exchanged at equilibrium was slightly higher than that of Ni^{2+} adsorbed, confirming the 100% ion-exchange mechanism of metal ion. To a lesser extent, the slight acidification resulting from the metal solution contributed to the release of some Ca^{2+} . In the case of other metal ions, such as Pb^{2+} , Hg^{2+} , Cu^{2+} , Cd^{2+} , Zn^{2+} , Mn^{2+} and Co^{2+} , the release of Ca^{2+} was less compared with the maximum quantity adsorbed onto the substrate. The total amount of metal adsorbed for these metals can be attributed to the surface adsorption processes and ion-exchange mechanism with other cations.

Experimental data are fitted to the Langmuir isotherm (Figure 2) by plotting $1/Q_e$ against $1/C_e$. Maximum adsorption capacity Q_0 and b values are given in Table 1. The maximum sorption capacity obtained from the Langmuir model increases in following the order: $\text{Cd}^{2+} < \text{Co}^{2+} \approx \text{Mn}^{2+} \approx \text{Ni}^{2+} < \text{Zn}^{2+} \approx \text{Hg}^{2+} < \text{Cu}^{2+} < \text{Pb}^{2+}$. Similar trends have also been observed by Gerente et al. (2000) and Reddad et al. (2002) for sugar beet pulp and Dupont et al. (2003) and Ravat et al. (2000) for wheat bran. In the case of biosorbents, the mode of sorption has been attributed to coulombic electrostatic interaction between anionic species of adsorbents and positively charged metal ions (adsorbates) and also to intrinsic adsorption based on the different sizes of adsorbent (Igwe and Abia, 2006). The natural organic materials are chemically heterogeneous, which creates difficulty in the prediction of interactions of organic matter with metal ions (Bouanda et al., 2002). The nonconventional lignocellulosic paddy straw consists of different polymers, such as cellulose (32 to 37%), hemicellulose (29 to 37%), lignin (5 to 15%), and other coextractives. Cai et al. (2007) characterized the rice straw (312 g/kg C, 5.8 g/kg N, and C/N = 54, 12.2% moisture). The polar functional carboxylic and hydroxyl ligands associated with the cell wall of the biosorbent in the present study could be involved in the chemical mechanism via biosorptive removal of many heavy metals.

Paddy straw has high water-holding capacity, as evidenced from the high porosity and high surface area in SEM images, which is one of the factors responsible for the sorption of many metal ions efficiently. The surface properties of the functional groups on cellulose could be modified by incorporation of other functional groups, and this also affects the adsorption capacity (Igwe and Abia, 2006). Wong et al. (2003) found that esterified tartaric acid on rice husk decreased 74 and 80% of copper and lead uptake, respectively, which indicated the necessity of carboxylic groups in the binding of metal ions. Lignin has a very high adsorption capacity towards

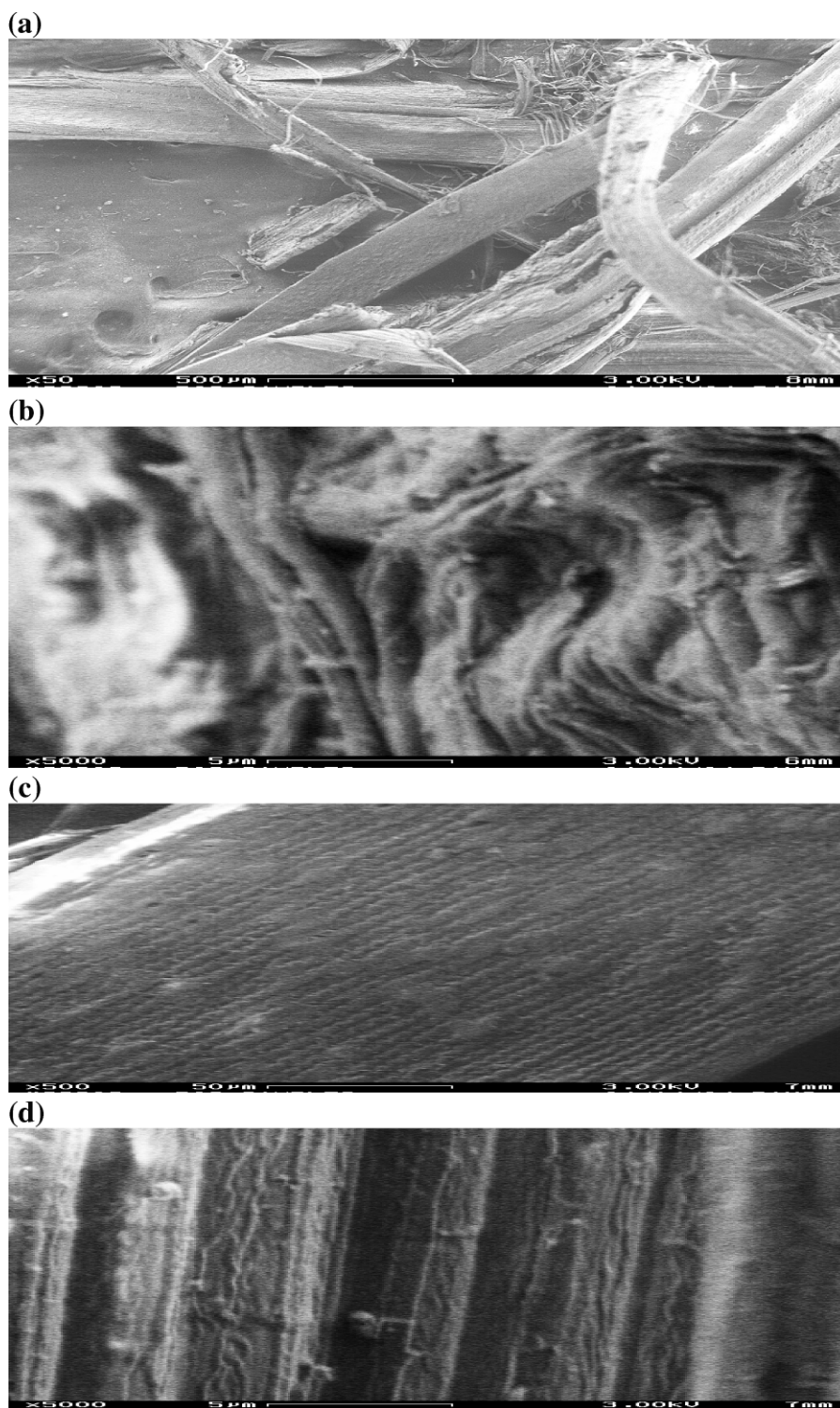


Figure 1—Scanning electron micrographs (LEO 982, Carl Zeiss Inc.) of the original paddy straw (a and b) and the sorbent (c and d) at different magnifications.

heavy metals, which is related to the activity of negatively charged surface and phenolic hydroxyl groups (Acemioglu et al., 2003; Lalvani et al., 1997). However, low-molecular-weight lignin molecules shield the carbohydrate (cellulose); hence, the lignocellulosic paddy straw needs prior processing to reduce the re-

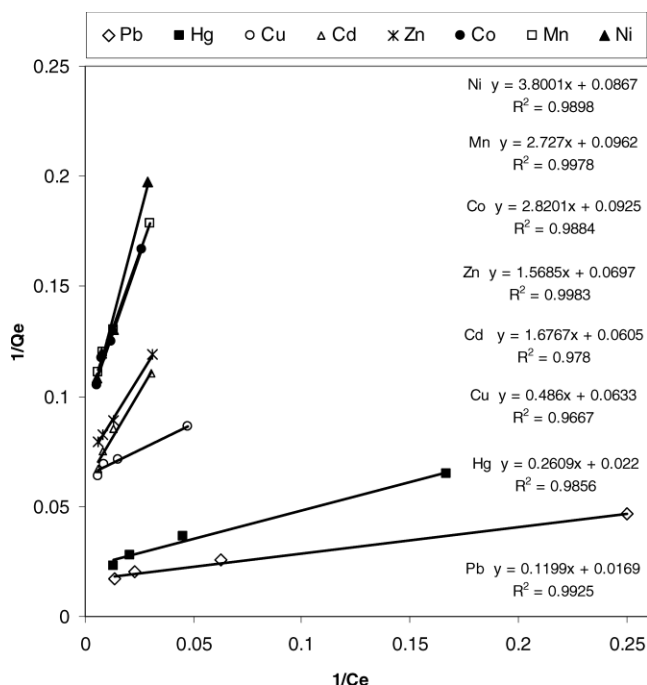
calcitrancy to the maximum possible extent and to render itself manually for more efficient biosorption (Krishnani and Ayyappan, 2006). In the present study, removal of low-molecular-weight lignin molecules through alkali treatment reduced the recalcitrancy of paddy straw, which enhanced the biosorption capacity.

Table 1—Metal ions sorption and corresponding Ca^{2+} release onto the lignocellulosic sorbent from paddy straw at pH = 6.5 (initial metal concentration 200 mg/L) and Langmuir coefficients applied to metal ions sorption.

Metal	Metal ion fixed		Ion exchange (IE)			Langmuir constants			
	mg/g	mmol/g	Ca^{2+} (mg/g)	Ca^{2+} (mmol/g)	% IE	Q_o (mg/g)	b (l/mg)	Q_o (mmol/g)	b (l/mmol)
Pb	58.8	0.284	7.18	0.179	63.1	59.17	0.141	0.286	29.2
Hg	43.75	0.218	1.82	0.045	20.8	45.45	0.084	0.226	16.9
Cd	14.9	0.133	3.97	0.099	74.5	16.52	0.036	0.147	4.06
Cu	15.6	0.245	8.24	0.206	83.7	15.79	0.13	0.248	8.27
Co	9.5	0.161	5.0	0.124	77.5	10.81	0.033	0.181	1.93
Mn	9.0	0.164	4.53	0.113	68.9	10.39	0.035	0.189	1.94
Zn	12.6	0.193	7.11	0.177	91.7	14.35	0.044	0.219	2.91
Ni	9.24	0.157	6.51	0.162	100	11.53	0.023	0.196	1.34
Cr*	21.5	0.413	6.1	0.152	36.8	—	—	—	—

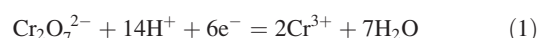
* pH = 2.

Biosorption data have been analyzed through interpretation of Dahlquist (1978) and Scatchard (1949) for the determination of binding site heterogeneity. A graphical representation of the Dahlquist (1978) and Scatchard (1949) interpretation has been obtained for eight different metal ions, by plotting Q_e/C_e versus Q_e , as shown in Figure 3. A straight line was obtained only for Ni^{2+} , which could prove an exclusive fixation by ion exchange on one type of site. This is also substantiated by the release of comparable moles of Ca^{2+} by the substrate. For other metal ions, the Scatchard plot presents a concave curve, which indicates the presence of two different types of sites, showing a negative cooperativity. These results are consistent with the work done by Gerente et al. (2000)

**Figure 2—Graphical representation of Langmuir isotherms for biosorption of heavy metal ions onto the lignocellulosic sorbent from paddy straw.**

for biosorption of Ni^{2+} and Pb^{2+} onto sugar beet pulp, with the exception of a convex curve for Cu^{2+} and with an interpretation of a single site binding with positive cooperativity.

Reduction of Hexavalent Chromium. Reduction of Cr^{6+} to Cr^{3+} and their subsequent adsorption onto the substrate at approximately pH 2 is shown in Figure 4, which indicates that reduction occurs slowly in the acidic solution. Initially, adsorption of Cr^{3+} was rapid and nearly 50% adsorption was reached in 24 hours. Thereafter, the approach to the equilibrium was slower, and saturation was reached only after 96 hours. This can be attributed to an increasing competition between protons and trivalent chromium toward surface sites. Gao et al. (2007) evaluated rice straw for the removal of Cr^{6+} at pH 2 for 48 hours of equilibration and observed that the amount of protons that disappeared in the solution was proportional to the amount of removed Cr^{6+} using rice straw. This is explained by the following reaction:



Functional groups (carboxylic and hydroxyl) present on the cellulose and lignin moieties in the biomass play an electron donor role in the Cr^{6+} to Cr^{3+} reduction mechanism. These results are consistent with the sugar-beet pulp reported by Reddad et al. (2003), who also found that Cr^{3+} ions are adsorbed onto the biosorbent by an ion-exchange mechanism, with Ca^{2+} cations neutralizing the carboxyl groups of the material.

Dupont and Guillon (2003) demonstrated the role of lignin moieties in the adsorption reaction of Cr^{6+} onto wheat bran. They identified that Cr^{6+} induces oxidation of lignin components and the retention of chromium ions occurs through a complexation reaction involving carboxylate moieties of lignin onto wheat bran. However, in the present study, most of the Ca^{2+} ions were released initially, as a result of acidification at pH 2 before adding Cr^{6+} (Figure 4). After 2 hours, the concentration of Ca^{2+} released was 19.4 mg/g (0.484 mmol/g), whereas adsorption of Cr^{3+} was only 5.82 mg/g (0.112 mmol/g). Subsequent Cr^{3+} adsorption and slight Ca^{2+} release suggest that Ca^{2+} is partly involved in ion exchange (36.8%) with Cr^{3+} . The adsorption of Cr^{3+} probably involves other ligands.

Gao et al. (2007) found the sorption capacity of rice straw for chromium removal to be 3.15 mg/g. They observed that carboxylic groups present on the biomass played an important role in both reduction and adsorption of chromium, and, because of Cr^{3+} binding, Cr^{6+} removal is promoted. In the present study, partially

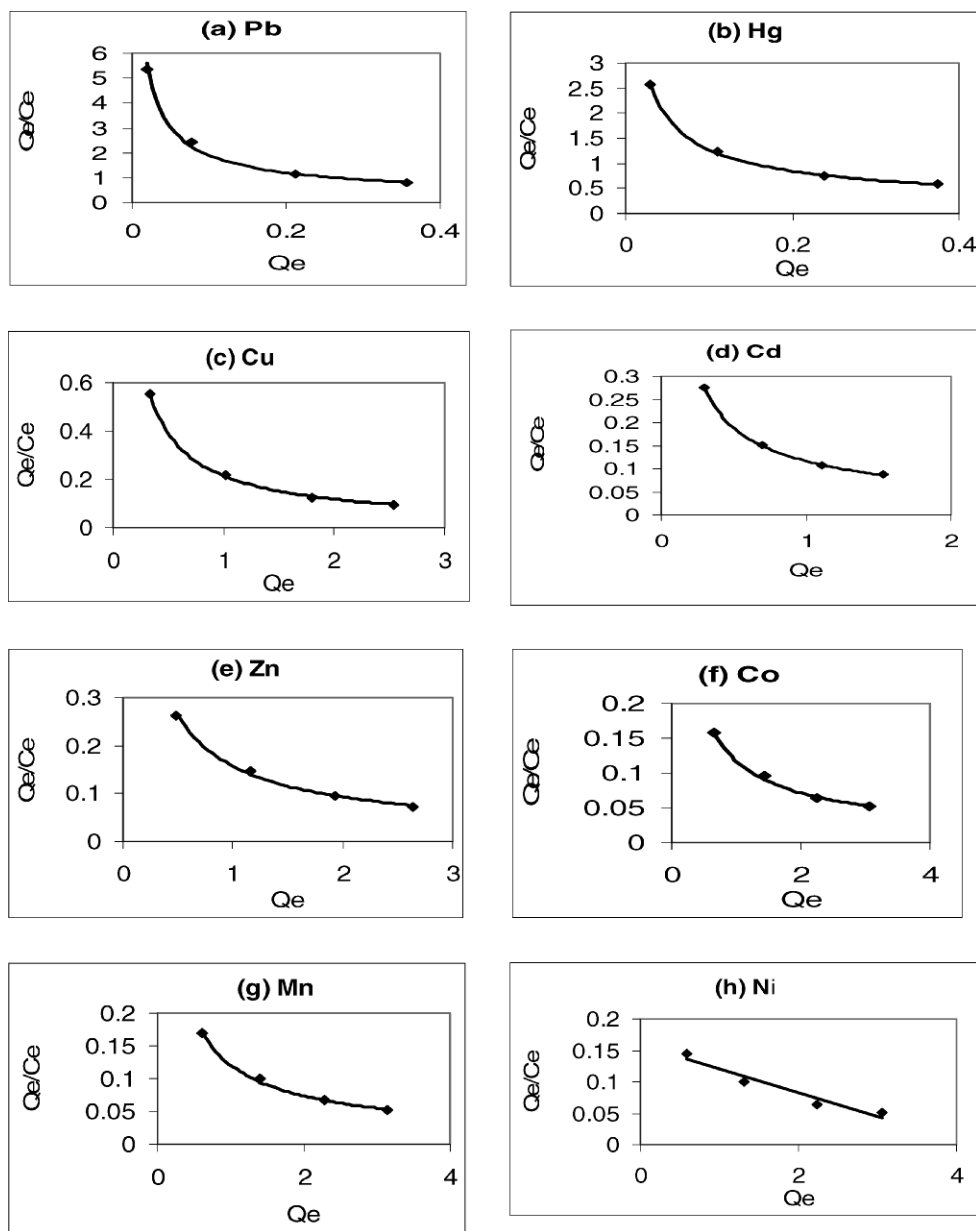


Figure 3—Scatchard plots of metal ions onto the lignocellulosic sorbent from paddy straw.

delignified paddy straw was found to adsorb 16.4 mg/g chromium in 48 hours and 21 mg/g chromium in 96 hours at pH 2. Lal (2002) also demonstrated a high degree of chromium adsorption (25 mg/g) for rice straw.

Krishnani et al. (2004) studied the efficacy of five different types of sorbent materials prepared from bagasse for detoxification of Cr^{6+} from coastal waters and found that acid-treated material is the most effective for detoxification of Cr^{6+} at low pH values, which has been attributed to the surface reduction of Cr^{6+} to Cr^{3+} , whereas the removal of Cr^{6+} in the treatment with other materials prepared from bagasse in an alkaline medium has been attributed to the reduction by an increase in the native microbial community in the coastal water.

Effect of pH on the Metal Sorption. The effect of pH on biosorption of the eight different metal ions onto lignocellulosic

product from paddy straw is shown in Figure 5, which indicates that sorption capacity increases with increasing pH. According to the surface complexation theory, complexation of metal onto lignocellulosic substrate is reduced at low pH values, as a result of increasing competition of protons with metal ions on the same binding sites. Typically, the pH of wastewater ranges from slightly acidic to neutral and slightly alkaline. Thus, pH 6.5 was maintained in the control and treatment, to ensure no formation of hydro-complexes resulting from chemical precipitation at constant ionic strength. For each metal, the adsorption pH (2, 4, of 6.5) was chosen to avoid the precipitation of the hydroxide $\text{M}(\text{OH})_2$. Most of the metal hydroxides get precipitated at pH 8 to 11.

In the case of Cr^{6+} reduction in acidic medium at pH 2, the reduction into Cr^{3+} mainly depends on the proton concentration and

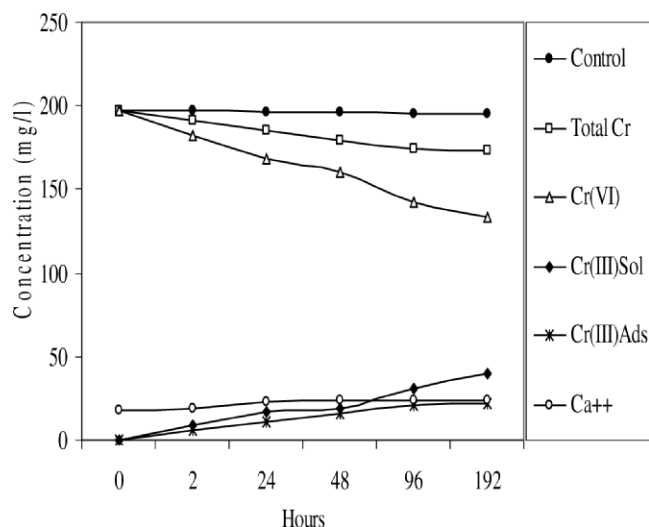


Figure 4—Reduction of Cr^{6+} to Cr^{3+} onto the lignocellulosic sorbent from paddy straw and release of Ca^{2+} at pH 2.

the involvement of lignin moieties as electron donors—the higher the proton concentration, the higher the efficiency of Cr^{6+} conversion. Such a dependence on proton concentration was also observed with anionic materials (Nakano et al., 2001). Gao et al. (2007) also found that protons are needed for the Cr^{6+} removal using rice straw at pH 2, as there was a decrease in chromium reduction with the increase of solution pH.

Speciation of Loaded Metal Ions Using X-Ray Photo Electron Spectroscopy. The XPS survey spectra of lignocellulosic product loaded with cadmium, mercury, and chromium are presented in Figures 6, 7, and 8. From this, it is evident that the lignocellulosic product consists of two major elements—carbon and oxygen. The presence of sorbed cadmium, mercury, and chromium have been detected on the lignocellulosic sorbent through the 3d5 peaks (406 to 410 and 413 to 417 eV) (Figure 6), 4f7 peak (103 to 110 eV) (Figure 7), and 2p peaks (576.3 and 587 eV) (Figure 8), respectively. The XPS spectra of these peaks reveal sorption of Cd^{2+} and Hg^{2+} onto the lignocellulosic product. The Cr 2p peaks consist of two contributions, corresponding to $2p^{1/2}$ and $2p^{3/2}$ energy levels, respectively. The XPS spectrum of chromium-treated substrate reveals an extensive reduction of Cr^{6+} sorbed onto substrate to its trivalent form, which compares well with the binding energies of Cr^{3+} in Cr_2O_3 at 576.3 and 586.2 eV, as reported by Boddu et al. (2003).

Leaching of Bound Metals. Leaching studies conducted with bound metal ions at different pH values revealed that leaching of heavy metals occurs at low pH values (1.8 ± 0.2) only. Approximately 70 to 88% and 28 to 37% bound metal ions were recovered from the metal-ion-loaded sorbent with aqueous solution of HNO_3 at pH 1.8 ± 0.2 and 4.2 ± 0.2 , respectively. However, except for Hg^{2+} (4%), there was no leaching of other metal ions at pH 6.3 ± 0.2 . Regeneration of the metal-loaded sorbent, though technically feasible, is not economical, as the sorbent is derived from abundantly available inexpensive lignocellulosic agrowaste.

Conclusions

Paddy straw is one of the most common agricultural wastes, with its main use as cattle feed. This agrowaste has not been used well

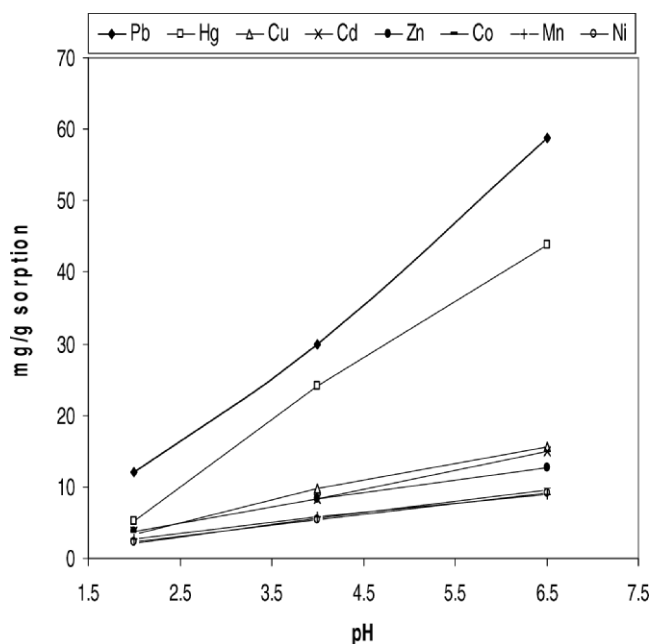


Figure 5—Effect of pH on the adsorption of metal ions onto the lignocellulosic sorbent from paddy straw.

yet. The use of paddy straw for metals remediation requires knowledge of its chemical reactivity and chelating surface sites, to determine its sorbent properties. In the present study, a lignocellulosic substrate from paddy straw has been harnessed for heavy metals removal. The sorption of heavy metals as a function of pH and metal concentration has been studied. The role of cations present in the substrate in ion exchange or adsorption or both has also been investigated. Sorption data have been analyzed using the Langmuir model and the Dahlquist (1978) and Scatchard (1949) interpretation. The unique ability of the biosorbent from paddy straw to bind nine different metals (Pb, Hg, Cd, Cu, Zn, Co, Mn, Ni, and Cr) has been attributed to the presence of heterogeneity and Ca^{2+} ions, which attract and sequester metal ions. Its relatively interesting sorption capacity could be related to the abundance of cellulose, lignin, and other functional moieties. Paddy straw is an environmentally friendly and cheap biosorbent, as it is mainly composed of macromolecules or natural polymers. Biosorption data and mechanistic information will be useful for the development of a new process involving this low-cost biosorbent.

Credits

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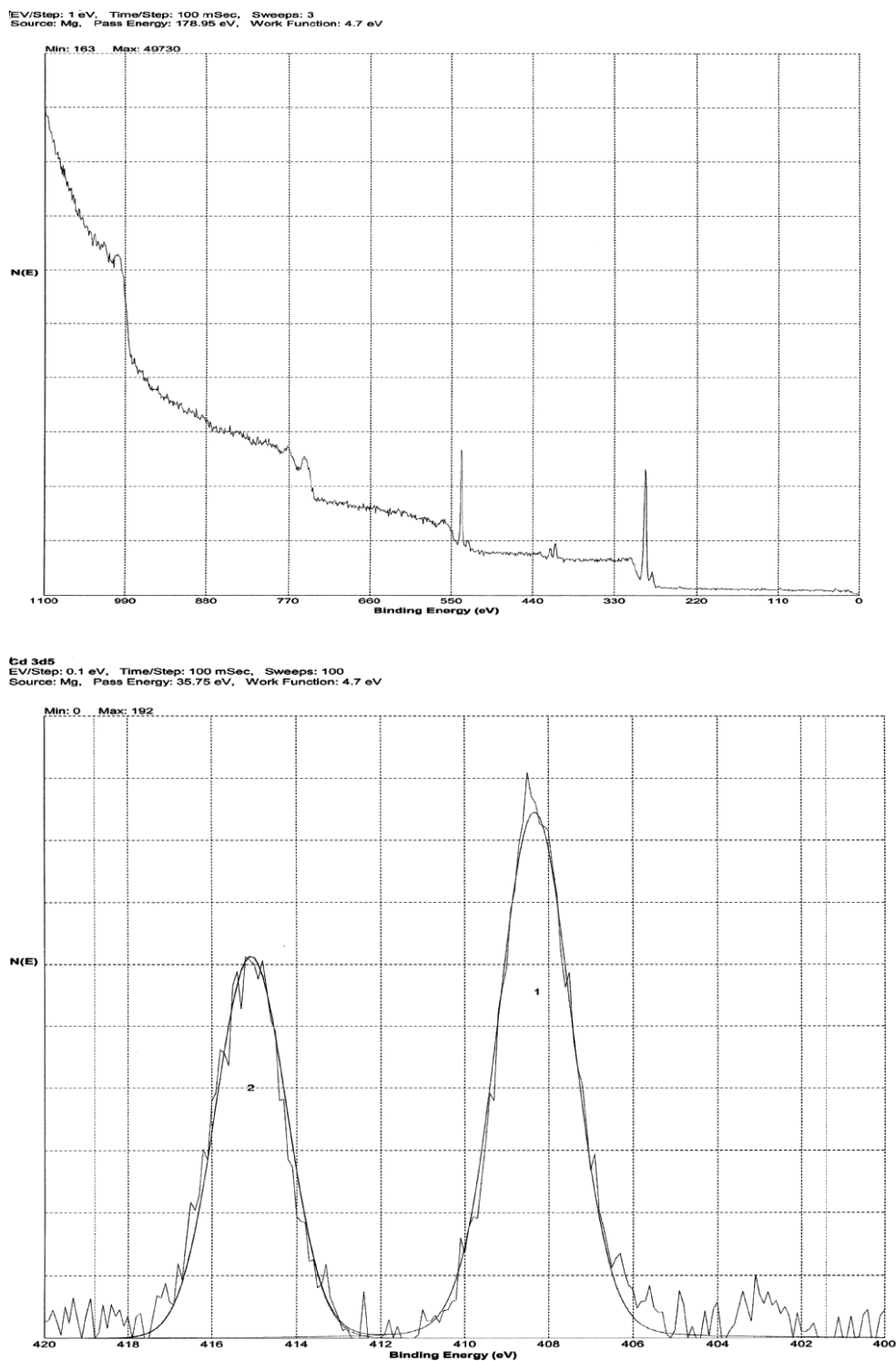


Figure 6—XPS of cadmium-loaded biosorbent.

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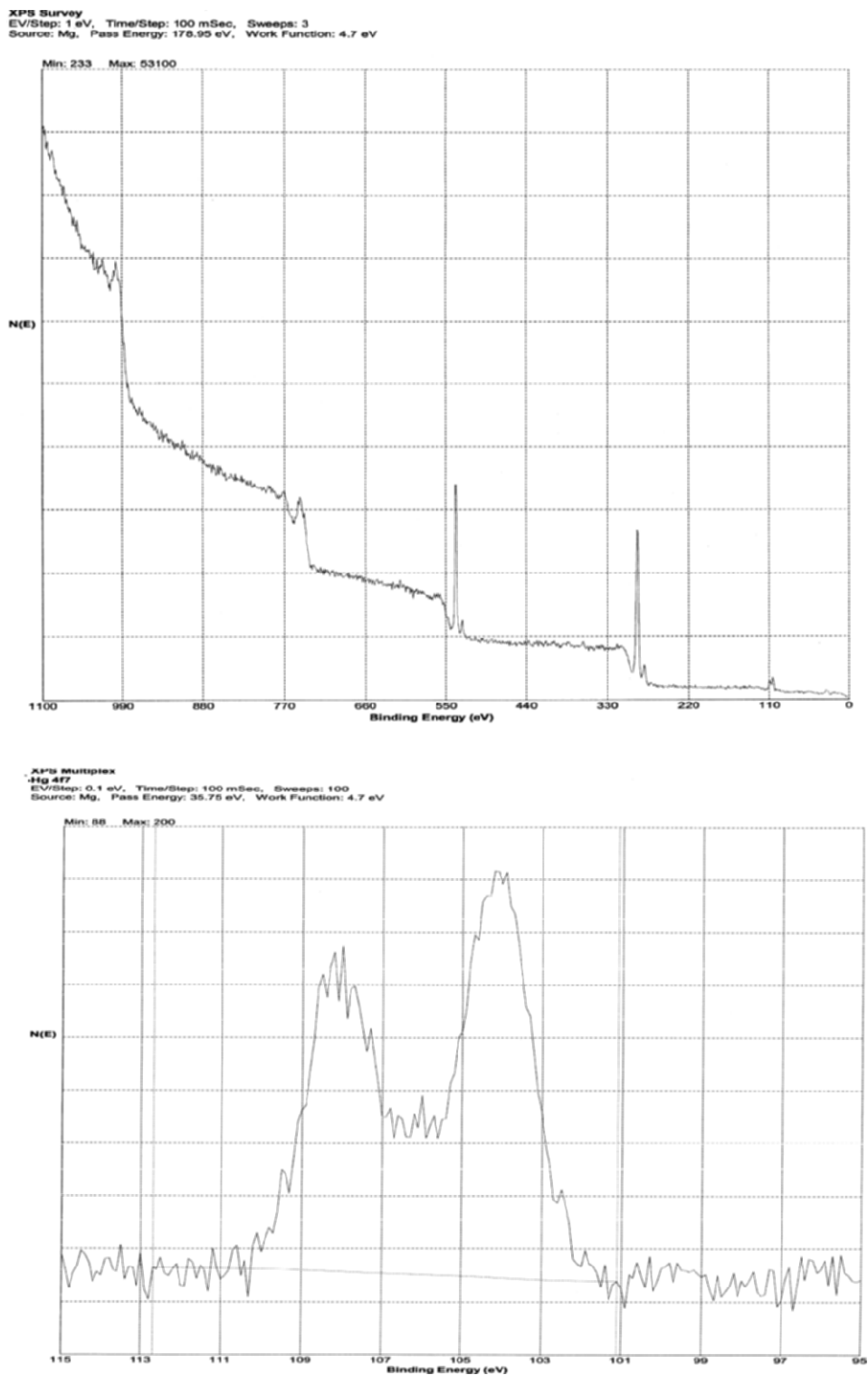


Figure 7—XPS of mercury-loaded biosorbent.

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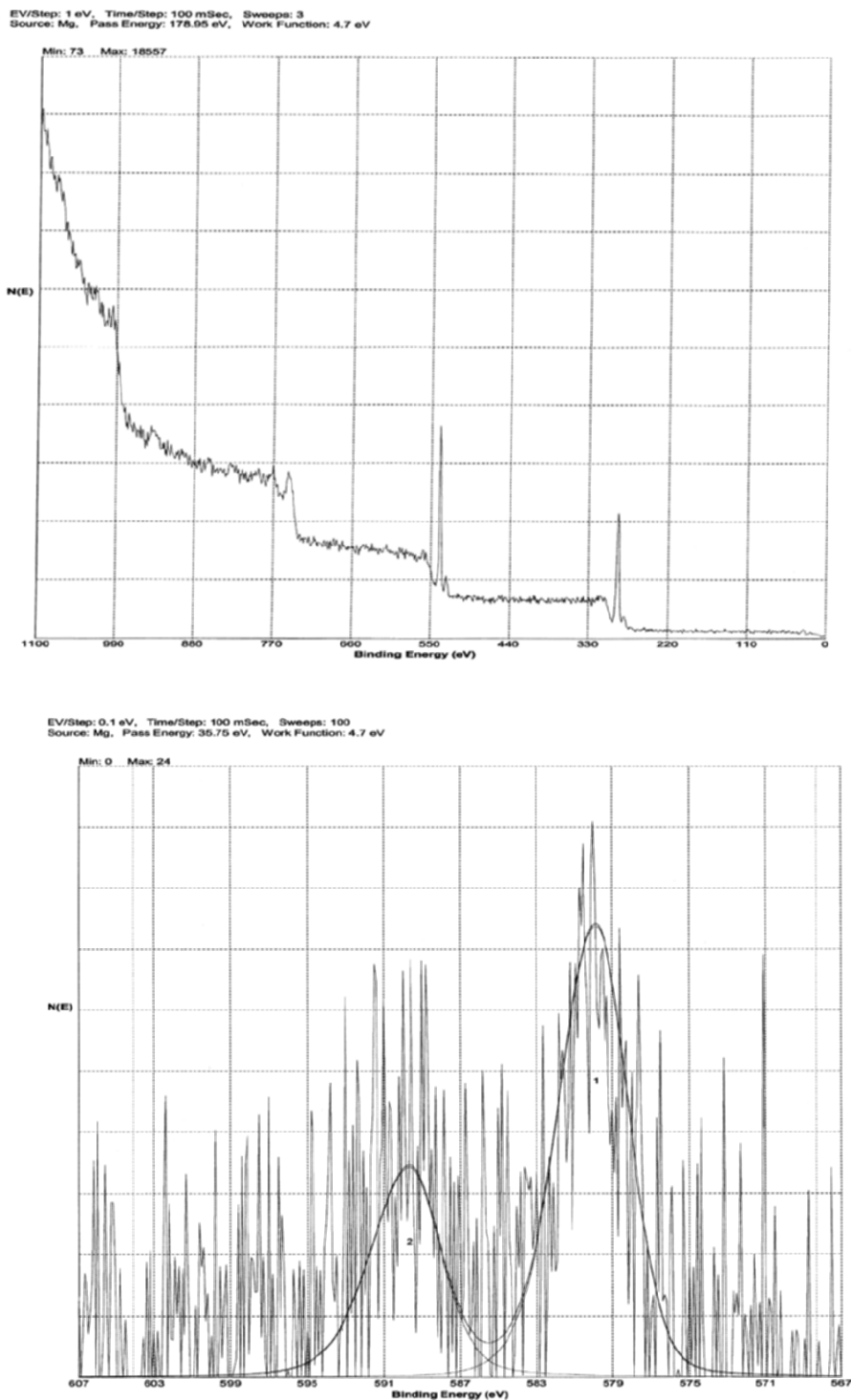


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