Biosorption mechanism of nine different heavy metals onto biomatrix from rice husk

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Abstract

A biomatrix was prepared from rice husk, a lignocellulosic waste from agro-industry, for the removal of several heavy metals as a function of pH and metal concentrations in single and mixed solutions. The biomatrix was characterized using scanning electron microscope and Fourier transform infrared spectroscopy, which indicated the presence of several functional groups for binding metal ions. Different experimental approaches were applied to show mechanistic aspects, especially the role of calcium and magnesium present in the biomatrix in ion exchange mechanism. The ultimate maximum adsorption capacity obtained from the Langmuir isotherm increases in the order (mmol/g): Ni (0.094), Zn (0.124), Cd (0.149), Mn (0.151), Co (0.162), Cu (0.172), Hg (0.18) and Pb (0.28). The sorption of Cr(III) onto biomatrix at pH 2 was 1.0 mmol/g. Speciation of chromium, cadmium and mercury loaded on the biomatrix was determined by X-ray photoelectron spectroscopy. The biomatrix has adsorption capacity comparable or greater to other reported sorbents.
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1. Introduction

During recent years, many researchers have focused their interest on heavy metals due to their known toxicity and carcinogenicity [1] as they are discharged in small quantities by numerous activities such as rapid industrialization, urbanization and anthropogenic sources into the environment [2]. There is a significant contamination of freshwater resources and an accelerating accumulation of toxic metals in the human food chain [3]. The removal of the toxic metal ions from water is a very difficult task due to the high cost of treatment methods. Various methods exist for the removal of toxic metal ions from aqueous solutions: reverse osmosis, ion exchange, chemical precipitation, electrodialysis, lime coagulation, adsorption using activated carbon and fly ash [4–12]. These techniques are not only expensive but also suffer with incomplete metal removal, high reagent and energy requirements, and generation of toxic

sludge [13]. In recent years, biosorption has been suggested as being cheaper and more effective than chemical (precipitation) or physical (ion exchange and membrane) technologies [14]. Biosorption involves the use of biological materials that form complexes with metal ions using their ligands or functional groups. Most metal sorption reported in literature is based on bacterial, algal and fungal biomass, which need to be cultured, collected from their natural habitats and pre-processed, with the result of additional costs [13]. The use of biosorbents from numerous lignocellulosic agrowastes is a very constructive approach and has received much attention in sorption of heavy metals, because they are inexpensive and have high adsorption properties resulted from their ion exchange capabilities [15–28]. Agricultural residues, especially rice husk, the by-product of the rice milling industry is produced in large quantities as a waste, creating environmental problems. Rice husk mainly consists of crude protein (3%), ash (including silica 17%), lignin (20%), hemicellulose (25%), and cellulose (35%) renders it suitable for metallic cations fixation. Rice husk has been used in the removal of some of the metal ions [29–32] but little attention has been paid to the biosorption of many metal ions together, metal speci-

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ation, involvement of functional groups and the identification of cations for ion exchange onto the biomatrix. In the present study, a biomatrix prepared from agrowaste—rice husk has been evaluated for the sorption of as many as eight metal ions Pb, Hg, Cd, Cu, Zn, Co, Mn and Ni as a function of pH and metal concentrations in single and mixed solutions and also for the reduction of Cr(VI) into Cr(III) in acidic medium. In addition to macroscopic metal sorption studies, SEM, XPS and FTIR were used to characterize the biomatrix, metal speciation and functional groups, respectively. Mechanistic aspects have been shown via different experimental approaches to determine the role of cations present in the biomatrix in ion exchange or adsorption or both.

2. Materials and methods

2.1. Chemicals

Deionized distilled water and carbonate free water were used to prepare all solutions and suspensions. Stock solutions of metal ions were prepared from their chloride ($CuCl_2 \cdot 2H_2O$, $HgCl_2$, $CdCl_2 \cdot 2.5H_2O$, $ZnCl_2 \cdot 7H_2O$, $MnCl_2 \cdot 4H_2O$, $NiCl_2 \cdot 6H_2O$, $CoCl_2$) or nitrate ($Pb(NO_3)_2$) salts. Cr(VI) was prepared from $K_2Cr_2O_7$. All metal standards were prepared by dissolving appropriate amount of metal salt into deionized water.

2.2. Preparation of biomatrix

Native rice husk (lignocellulosic substrate) was obtained from agro-industry and was subjected to 1.5% alkali treatment (300 g in 1 L) and then autoclaved at 121 °C for 30 min in order to remove the low molecular weight lignin compounds. After filtration, this material was washed with deionized water until the pH reached a constant value close to neutrality. This fraction was then filtered off and dried in oven at 50 °C.

2.3. Characterization of the biomatrix

Surface morphology was studied with the scanning electron microscope (LEO 986 field emission gun, Carl Zeiss Inc., Thornwood, NY). Micrographs of biomatrix were obtained using double-sided carbon tape.

2.4. Equilibrium adsorption isotherms (batch experiment)

Equilibrium isotherm studies were conducted at 32 ± 0.5 °C with constant amount of biomatrix (3 g/L) at the constant pH 6 ± 0.1 (except for Hg and Cu at pH 5.5 ± 0.1) to evaluate the biomatrix for the removal of different metal ions separately. Prior to the introduction of the metal ions, the flasks were vigorously stirred for 1.5 h to hydrate the biomatrix, which either naturally buffered solution pH or adjusted with HNO_3 at 5.5–6.0. After the introduction of the initial concentrations of metal ions in the range of 50–200 mg/L, samples were collected at suitable time intervals for 180 min and filtered through 0.45 μm membrane filter and then analyzed for metal and calcium elements with an inductively coupled plasma

(ICP) emission spectrometer (Varian Liberty-200, Palo Alto, CA).

In order to study the metal removal mechanism, another experiment was conducted with a low initial concentration (80 mg/L) of Pb^{2+}, Hg^{2+} and Cd^{2+}, respectively, for a constant biomatrix concentration equal to 3.0 g/L at the constant pH 6 ± 0.1. Prior to the introduction of the metal ions, the flasks were vigorously stirred for 1.5 h to hydrate the biomatrix and then required volume of the aqueous solution was filtered through 0.45 μm filter and filtrate was analyzed for initial Ca^{2+}, Mg^{2+} and Na^+ ions released by the biomatrix. Metal solution was allowed to equilibrate with the biomatrix in an incubator agitated at 200 rpm for 180 min. After equilibration, the metal ion solution was filtered using 0.45 μm filter and filtrate was analyzed for the concentrations of metals and for the Ca^{2+}, Mg^{2+} and Na^+ ions released by the biomatrix using inductively coupled plasma (ICP) emission spectrometer (Varian Liberty-200, Palo Alto, CA).

Reduction of Cr(VI) experiment was performed according to the batch method at 32 ± 0.5 °C. First sample was introduced in 400 mL of deionized water. Prior to the introduction of the metal ions, the flasks were vigorously stirred for 1.5 h to hydrate the biomatrix and the initial pH was adjusted to 2.0 with HNO_3. After the desired temperature was attained, known amount of Cr(VI) was introduced. Then the flask was agitated in incubator and samples were collected at suitable time intervals, filtered through a 0.45 μm filter. Filtered solutions were analyzed for hexavalent and total chromium. Cr(VI) was detected by the diphenyl carbazide method [33]. The concentration of Cr(VI) was calculated from the absorbance at 542 nm using a UV–vis spectrophotometer. Total chromium was determined by an inductively coupled plasma spectrometer (Varian Liberty 200, Palo Alto, CA). The difference in concentration between total and Cr(VI) was taken as the concentration of trivalent chromium.

The amount of the metal adsorbed (mg) per unit mass of biomatrix (Q_e) was obtained by using the equation

$$Q_e = \frac{(C_i - C_e)V}{M}$$

where C_i and C_e are the initial and equilibrium concentrations in mg/L, M the dry mass of biomatrix in grams and V is the volume of solution in litres.

2.5. Effect of pH

The adsorption of metal ions was studied over a pH range of 2–7. For each metal, the adsorption pH was chosen to avoid the precipitation of the hydroxide $M(OH)_2$. In order to evaluate the pH profile of the adsorption process, metal solutions at different pHs were allowed to equilibrate with the biomatrix in an incubator agitated at 200 rpm at 32 ± 0.5 °C. After equilibration, the biomatrix was filtered from the solution using 0.45 μm filter and filtrate was analyzed for metals.

2.6. Adsorption isotherms

To find out the mechanistic parameters associated with metal ion adsorption, the results were analyzed by Langmuir and Freundlich isotherms. The mathematical expression of the Langmuir isotherm is

$$Q_e = \frac{Q_0 b C_e}{1 + b C_e}$$

$$\frac{1}{Q_e} = \frac{1}{Q_0} + \frac{1}{b Q_0 C_e}$$

where C_e is the equilibrium concentration of the adsorbate in solution (mg/L), Q_e the equilibrium loading of sorbate on sorbent (mg/g), Q_0 and b are the Langmuir constants related to maximum adsorption capacity (mg/g), and the relative energy of adsorption (L/mg), respectively.

The logarithmic form of the Freundlich model is given by the equation

$$\log \, Q_e = \log \, K_f + \frac{1}{n} \log C_e$$

where Q_e is the amount adsorbed (mg/g), C_e the equilibrium concentration of the adsorbate(mg/L) and K_f and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

2.7. Column adsorption experiment

The results obtained from batch experiments adsorption were used to remove metal ions by column. Continuous column adsorption experiments were conducted to evaluate biomatrix for the removal of eight different metal ions in combination. Heavy metals such as Pb, Hg, Cd, Cu, Ni, Co, Mn and Zn were spiked in the deionized water (final concentration of each metal 12.5 mg/L). Column flow experiment was conducted in a glass column of dimension; 1 cm internal diameter by 15 cm length. Columns ends were fitted with filter disk (millipore) to retain the material. The weighed biomatrix (2 g) was used to pack the column up to 10 cm. Column was shaken while being packed with dried biomatrix to minimize void volumes and air gaps. The column was kept undisturbed for its full settlement and saturation. Concentrations of column effluents obtained at various time intervals were monitored using inductively coupled plasma spectrometer. The bed volume of the column was 12 mL. The flow rate was varied (0.2–2 mL/min) to achieve the maximum uptake of metal ions by the biomatrix. The column runs were carried out to the point where the breakthrough was observed for most of the metals.

2.8. X-ray photoelectron spectroscopy of biomatrix

X-ray photoelectron spectroscopy (XPS) was used to characterize the surface chemistry of the lingocellulosic biomatrix. Information was obtained on the elemental composition of the surface to a depth of about 0.1–1 nm. XPS spectra of the biomatrix were obtained on a PHI model 5400 axis Ultra Kratos

Analytical instrument (Manchester, UK). 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. The powdered samples were mounted on the double-sided carbon tapes. Binding energies were calibrated by assuming 284.6 eV for the C–C component of the C 1s line. Biomatrix loaded with chromium, cadmium and mercury were also analyzed by XPS.

2.9. Fourier transform infrared spectroscopy of biomatrix

In order to determine the functional groups responsible for metal binding, biomatrix was analyzed using a Fourier transform infrared spectrometer-FT/IR 4100 (Jasco Corp., Tokyo, Japan) in the range of 500–4000 cm^{-1}.

3. Results and discussion

3.1. Characterization of the biomatrix using scanning electron microscopy

The SEM images of lignocellulosic biomatrix prepared from rice husk are shown in Fig. 1. The SEMs at different magnifi-
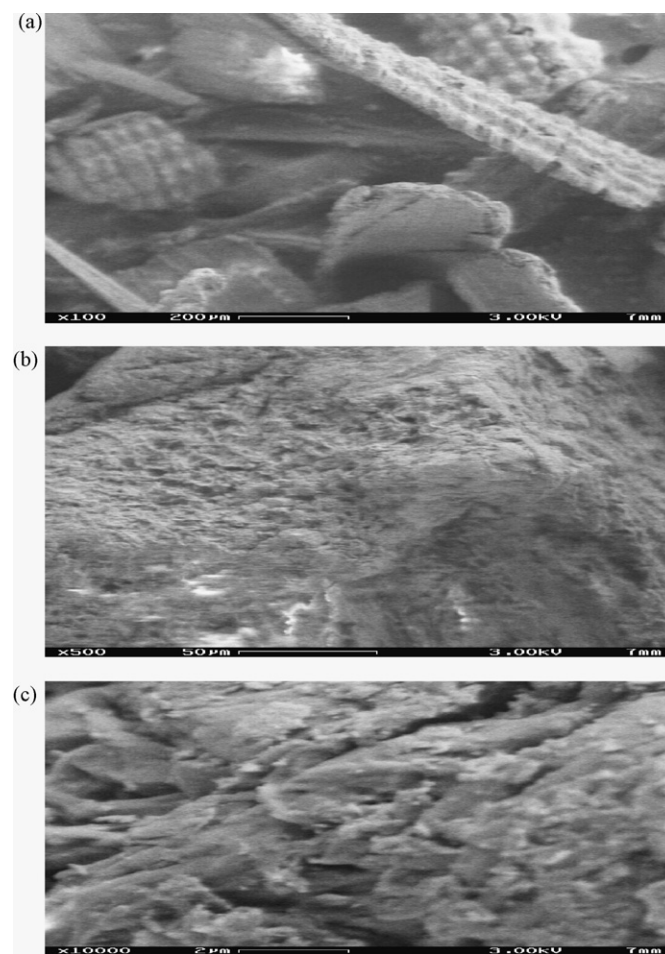

Fig. 1. Scanning electron micrographs (LEO 982, Carl Zeiss Inc., Thornwood, NY) of the biomatrix from rice husk at different magnifications: (a) 100×, (b) 500×, (c) 10,000×.

Table 1

Maximum adsorption capacities and corresponding Ca^{2+} release for biomatrix in the present study with initial metal concentration 200 mg/L at pH 6 ± 0.1 (except Hg and Cu at pH 5.5 ± 0.1) and other lignocellulosic materials in the literature (mg/g)

Material	Cd	Cr(VI)	Pb	Zn	Cu	Ni	Hg	Co	Mn	Literature
Sugar beet pulp	24.4	–	73.76	17.8	21.1	11.8	–	–	–	[19–22]
Sugar beet pulp	–	10[a]	–	–	–	–	–	–	–	[23]
Sugar beet pulp	–	–	60	–	30	12	–	–	–	[38]
Sugar beet pulp	–	17.2	–	–	–	–	–	–	–	[50]
Saw dust	–	39.7	–	–	–	–	–	–	–	[50]
Bagasse	–	13.4	–	–	–	–	–	–	–	[50]
Wheat bran	–	35	–	–	–	–	–	–	–	[24]
Rice husk	–	–	108	–	29	–	–	–	–	[51]
Rice husk	4	–	45	–	–	–	–	–	–	[52]
Rice husk	21.3	164.3	11.4	–	–	–	–	–	–	[53]
Coconut husk fibres	–	29	–	–	–	–	–	–	–	[54]
Palm-pressed fibres	–	15	–	–	–	–	–	–	–	[54]
Bio-adsorbent (mg/g)	14.4	52.1[a]	54	7.47	10.8	5.4	33.1	8.5	7.7	Present study
Bio-adsorbent (mmol/g)	0.128	1.00[a]	0.261	0.114	0.169	0.091	0.165	0.144	0.136	
Ca^{2+} (mg/g)	4.13	–	5.42	3.05	7.04	3.96	2.06	4.97	3.17	
Ca^{2+} (mmol/g)	0.103	–	0.135	0.076	0.175	0.099	0.051	0.124	0.078	
%Ca^{2+} exchange	80.5	–	51.7	66.7	100	100	31.1	86.1	57.3	

[a] Cr(III).

cations of 100×, 500× and 10,000× do not reveal any apparent surface deformations due to the partial alkaline digestion. This shows the physical integrity of the biomatrix.

3.2. Kinetics of metal ions(II) removal

Studies conducted on the kinetics of metal ions(II) removal revealed that the majority of metal ions were removed within the first 90–120 min contact with the biomatrix. The equilibrium state was reached after 120–150 min contact time.

3.3. Equilibrium isotherm

Results of the equilibrium adsorption isotherm for the initial metal concentration of 200 mg/L and corresponding release of Ca^{2+} at 32 ± 0.5 °C and pH 6 ± 0.1 (except for Hg and Cu at pH 5.5 ± 0.1) are shown in Table 1. The maximum sorption capacity (MAC) experiment at initial metal concentration of 200 mg/L showed that chemically digested agrowaste was able to bind the following amounts of metals in mg metal/g biomatrix: 54 mg Pb/g, 33.1 mg Hg/g, 14.4 mg Cd/g, 10.8 mg Cu/g, 8.5 mg Co/g, 7.47 mg Zn/g, 7.7 mg Mn/g and 5.4 mg Ni/g. Maximum values of adsorbed per unit mass of adsorbent reported in the literature are given in Table 1. The values from present study are comparable or considerably greater than other reported lignocellulosic sorbents. Furthermore, these values are higher than adsorption capacities previously reported with activated carbon cloth (0.12–0.13 mmol/g) and granular activated carbon (0.06–1.02 mmol/g) for the removal of Pb^{2+}, Cu^{2+} and Ni^{2+} [34].

The ratio qm-Ca^{2+} released/qm-metal fixed expressing the percentage of ion exchange (or adsorption) indicates that relating to Ca^{2+} ions, a comparable quantity was released from the material, confirming the ion exchange mechanism of metal species. In the case of Cu^{2+} and Ni^{2+}, the amount of Ca^{2+} exchanged was slightly higher than the metal ion adsorbed. To a lesser extent, the slight acidification due to the metal solution contributed to

the release of some Ca^{2+}. This indicates that rice husk contains enough carboxylic moieties to bind with the Ca^{2+} ions. In the case of other metal ions such as Pb^{2+}, Hg^{2+}, Cd^{2+}, Zn^{2+}, Mn^{2+} and Co^{2+}, the release of Ca^{2+} was not comparable with the maximum quantity adsorbed onto the biomatrix. There might be other cations involved in the ion exchange. Hence, another batch experiment was conducted for initial metal concentration of 80 mg/L for Pb^{2+}, Hg^{2+}, Cd^{2+} at 32 ± 0.5 °C and pH 6 ± 0.1. Results are given in Table 2a, which indicates that apart from Ca^{2+}, Mg^{2+} ions are also involved in ion exchange process, especially in the case of Hg^{2+}. Before adding metals into the solution, motions of Na^{+} ions into the solution was in the same order of magnitude, which revealed that Na^{+} are loosely bound ions and seem to be independent of the metal ion concentration.

Biomatrix from rice husk is constituted by lignin and cellulose as its major constituents, bearing functional groups such as alcohol, ketones and carboxylic groups that can be involved in complexation reactions with metallic cations. Reddad et al. [20] conducted studies on the Ni^{2+} and Cu^{2+} binding properties of native and modified sugar beet and they found that the chemical modifications applied to the native material resulted in an improvement of the cation exchange capacities. Due to the loss of all methoxyl groups from the carboxylic moieties, base extracted pulp and saponified pulp exhibited the highest Ni^{2+} and Cu^{2+} ion uptake among the materials tested.

Table 2a

Metal ions sorption and corresponding ion exchange onto the biomatrix at pH 6.0 ± 0.1 (initial metal concentration 80 mg/L)

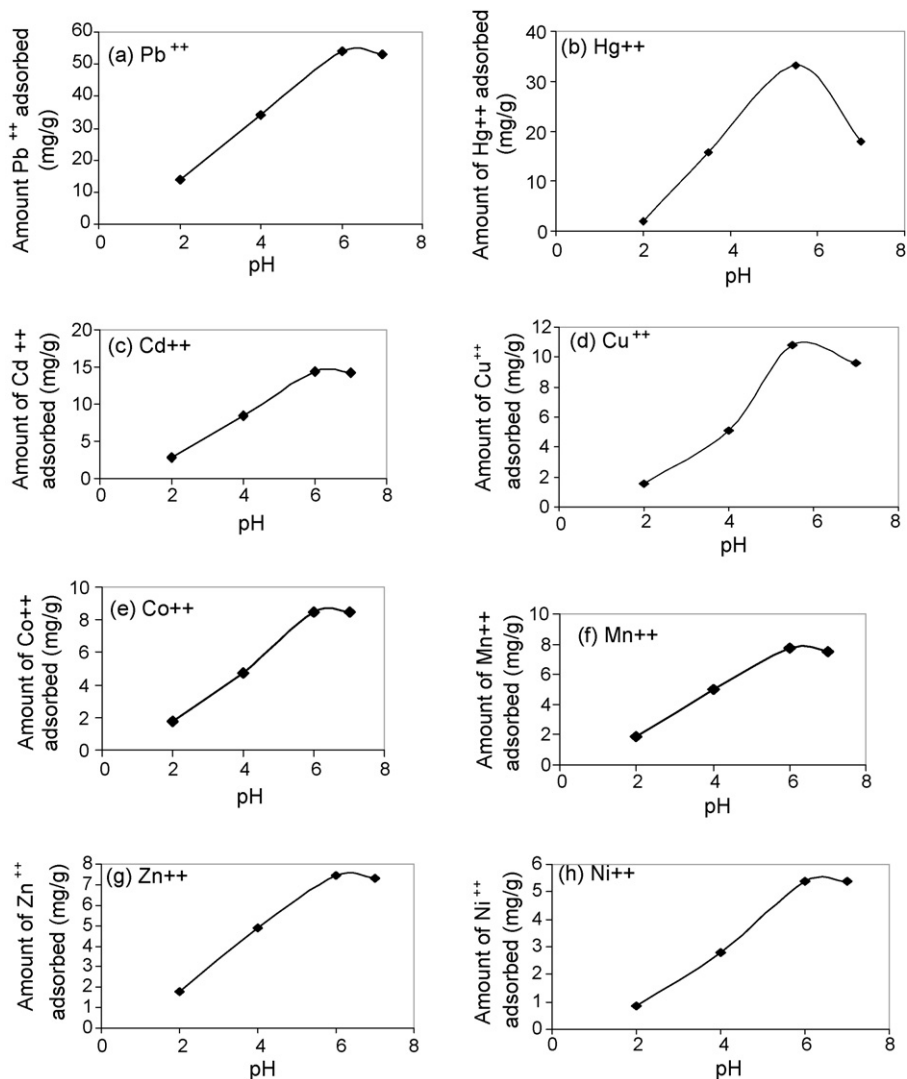| Metal	Metal ion fixed		Exchangeable ions (mmol/g)		
	mg/g	mmol/g	Ca^{2+}	Mg^{2+}	Total
Pb	28.1	0.135	0.078	0.059	0.137
Hg	18.9	0.094	0.034	0.037	0.071
Cd	9.7	0.086	0.0738	0.0185	0.092

Fig. 2. Effect of pH on the adsorption of metal ions onto biomatrix.

Work done by Baig et al. [35] on the binding of Pb^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+}, Cr^{3+} and Cr^{6+} to the inactivated biomass of *Solanum elaeagnifolium* has suggested that to some extent carboxyl groups (−COOH) are responsible for the binding of metal ions and at lower pHs, the carboxyl groups retain their protons reducing the probability of them binding to any positively charged ions, whereas at higher pHs (above 4.0), the carboxyl groups are deprotonated with the result of negatively charged ligands (−COO⁻), which attract the positively charged metal ions and binding occurs. Thus, metal ion binding to the biomass is an ion exchange mechanism, which involves electrostatic interaction between metallic cations and the negatively charged groups in the cell walls [36]. This indicates that metal binding can be enhanced by increasing the number of carboxylate ligands in the biomass. Baig et al. [35] also observed that the biomass binds more than 80% of Pb^{2+} at pH 3.0 and about 50% at pH 2.0, and suggested that besides carboxyl groups, other groups may also be involved in Pb^{2+} binding. However,

they also observed that modification did not lead to any significant difference in Cd^{2+} binding, and suggested the possibility of involvement of other ligands in the binding of Cd^{2+} to the biomass. In the present study, the amount of metal bound to the biomass increases with increasing concentration of metal in the solution. Further increase in the metal concentrations does not lead to an increasing amount of bound metal, since all binding sites are already saturated with metal.

Studies conducted by Gerente et al. [37] on the effect of organic load composed of single molecules of benzaldehyde, benzoic acid and phenol, revealed that the presence of only benzoic acid reduces the fixation of Cu^{2+} from about 30%, this was attributed to the complexation of Cu^{2+} and benzoic acid in the solution, which prevented the Cu^{2+} to be fixed on the pulp. The present results confirm the strong affinity of Pb^{2+}, Cu^{2+} and Hg^{2+} ions onto the biomatrix, it is obvious that Ni^{2+} ions are the least fixed ($Q_e = 0.091$ mmol/g) followed by Zn^{2+} ($Q_e = 0.114$ mmol/g).
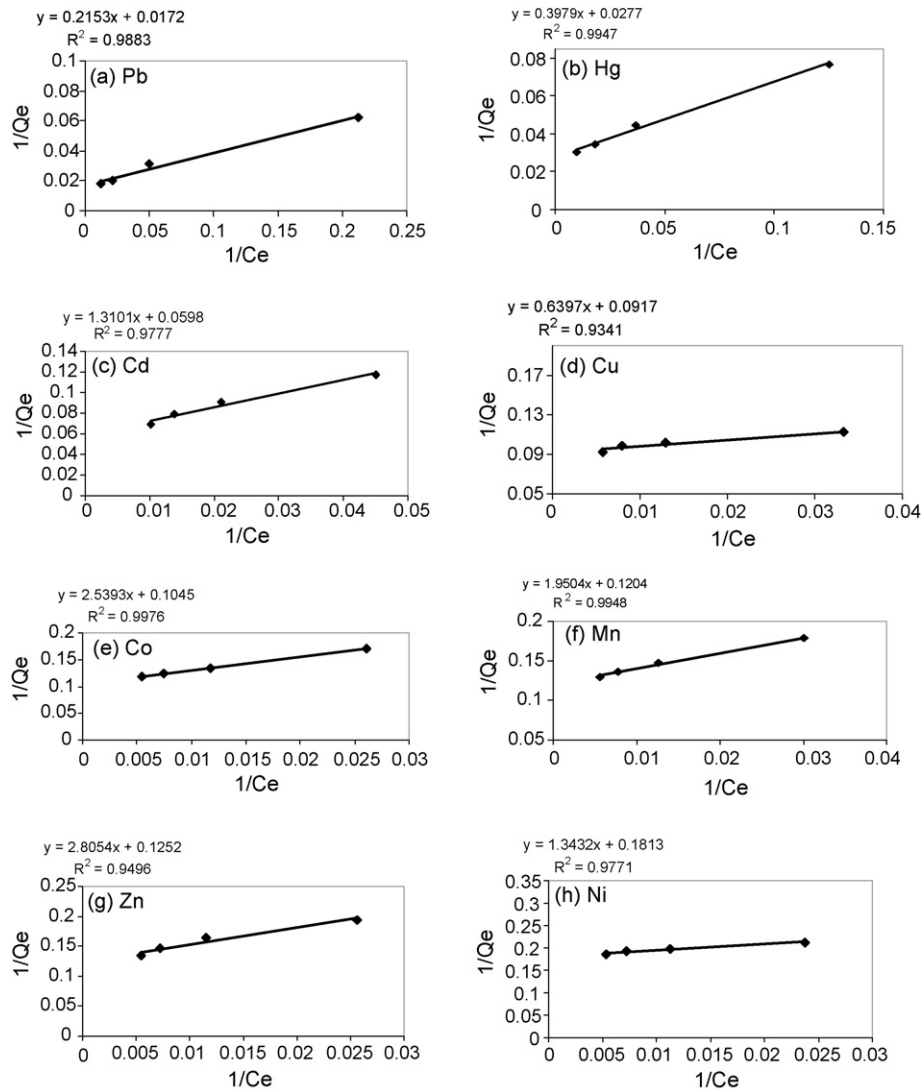
Fig. 3. Graphical representation of Langmuir isotherms for heavy metal ions.

3.4. Effect of pH on metal sorption

The pH of the aqueous solution is an important controlling parameter in the heavy metal adsorption processes. Its role on the removal of metal ions was studied by varying the initial concentration of nitric acid in the suspension. The binding of metal ions to lignocellulosic biomatrix as a function of pH (2–7) is shown in Fig. 2. Figure demonstrates that metal binding is strongly pH dependent with more metal cations bound at higher pH and the maximum uptake of metal ion took place at pH $5.5–6 \pm 0.1$. According to the surface complexation theory, the increase in metal removal as pH increases can be explained on the basis of a decrease in competition between proton and metal species for the surface sites and by the decrease in positive surface charge. For metal ions (except Hg^{2+}), there was a slight decrease in metal removal in pH higher than 5.5–6. For each metal, the adsorption pH $((5.5–6) \pm 0.1)$ was chosen to avoid the precipitation of the metal hydroxides. However, decrease in Hg^{2+} removal at higher pH (7) was significant, due to the major role of Mg^{2+} ions in an ion exchange process, which might be inhibited due to the

hydroxide formation of mercury. However, for other metal ions, a higher pH range (Pb 8.0–8.5, Cd ~11, copper ~8.1, nickel ~10.8, and zinc ~10.1) and higher initial metal concentrations are required for any appreciable precipitation. Metal binding by biomatrix is reduced at low pH values due to increasing competition of protons for the same binding sites that metals can use.

3.5. Langmuir and Freundlich isotherms

Langmuir and Freundlich isotherms are used to represent adsorption of components from liquid phase on to a solid phase. In Langmuir isotherm, when $1/Q_e$ is plotted against $1/C_e$, a straight line with slope $1/bQ_0$ is obtained (Fig. 3). In Freundlich isotherm, when $\log Q_e$ is plotted against $\log C_e$, a straight line with slope $1/n$ is obtained (Fig. 4). Values of the parameters of the isotherms are reported in Table 2b. The isotherms indicate that adsorption increases with an increase in equilibrium concentration of the sorbate. Adsorption follows both Langmuir and Freundlich isotherms (Figs. 3 and 4). However, the equi-
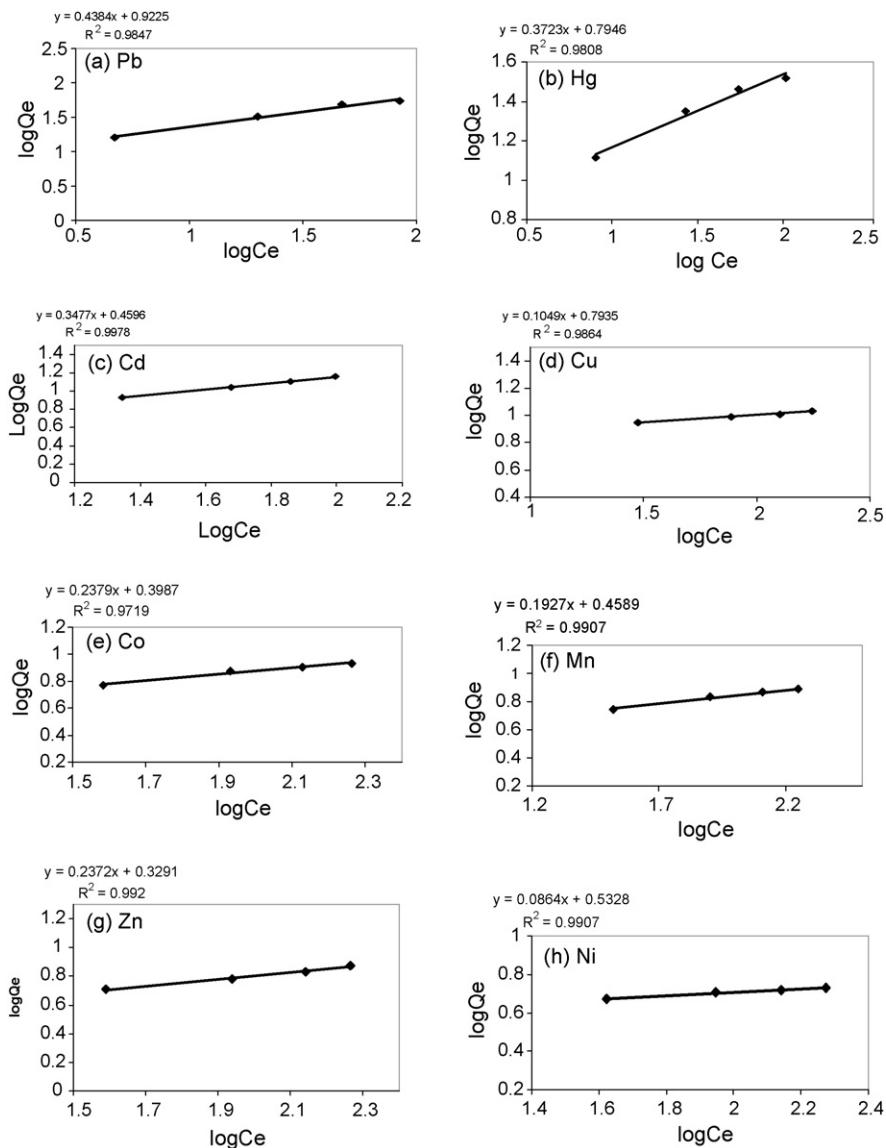
Fig. 4. Graphical representation of Freundlich isotherms for heavy metal ions.

librium data fitted well with the Langmuir adsorption isotherm. To ultimate capacity obtained from the Langmuir model is mg/g and mmol/g biomatrix, which increases in the order: $Ni^{2+} < Zn^{2+} \approx Cd^{2+} \approx Mn^{2+} \approx Co^{2+} < Cu^{2+} \approx Hg^{2+} < Pb^{2+}$.

Table 2b
Langmuir and Freundlich coefficients applied to metal ions sorption onto the biomatrix

Metal ion fixed	Langmuir constants				Freundlich constants	
	Q_0 (mg/g)	b (l/mg)	Q_0 (mmol/g)	b (l/mmol)	K_f	n
Pb	58.1	0.08	0.28	16.55	8.36	2.23
Hg	36.1	0.069	0.18	13.84	6.23	2.67
Cd	16.7	0.052	0.149	5.84	2.88	2.88
Cu	10.9	0.143	0.172	9.11	6.21	9.53
Co	9.57	0.041	0.162	2.42	2.5	4.2
Mn	8.30	0.062	0.151	3.406	2.88	5.19
Zn	8.14	0.045	0.124	2.94	2.13	4.21
Ni	5.52	0.135	0.094	7.92	3.41	11.57

This can be attributed to adsorption combined with ion exchange mechanism and, ionic attraction of positively charged metal ions and negatively charged carboxylic groups. Similar trends have also been observed by Gerente et al. [38] and Reddad et al. [19] for sugar beet pulp and Dupont et al. [25] and Ravat et al. [39] for wheat bran.

For metal ions, the stability of the complexes is determined largely by the basicity of the donor group, i.e. the availability of the electron, the greater the basicity, the greater the stability of the complex [40]. Copper is known to form complexes with very high stability despite a poor basicity of the donor group [40], fixation depends on the metal ion, on its chemistry and its affinity to the ligand. Two types of fixation sites would coexist: the carboxylic sites involved in ion exchange and those taking part in adsorption. Furthermore, fixation capacities are dependent on the metals sorbed, it is higher with Pb^{2+} due to its strong affinity with carboxylic functions onto the substrate and decreasing with Cu^{2+} and Ni^{2+} [38] with the result of fixation capacities in the
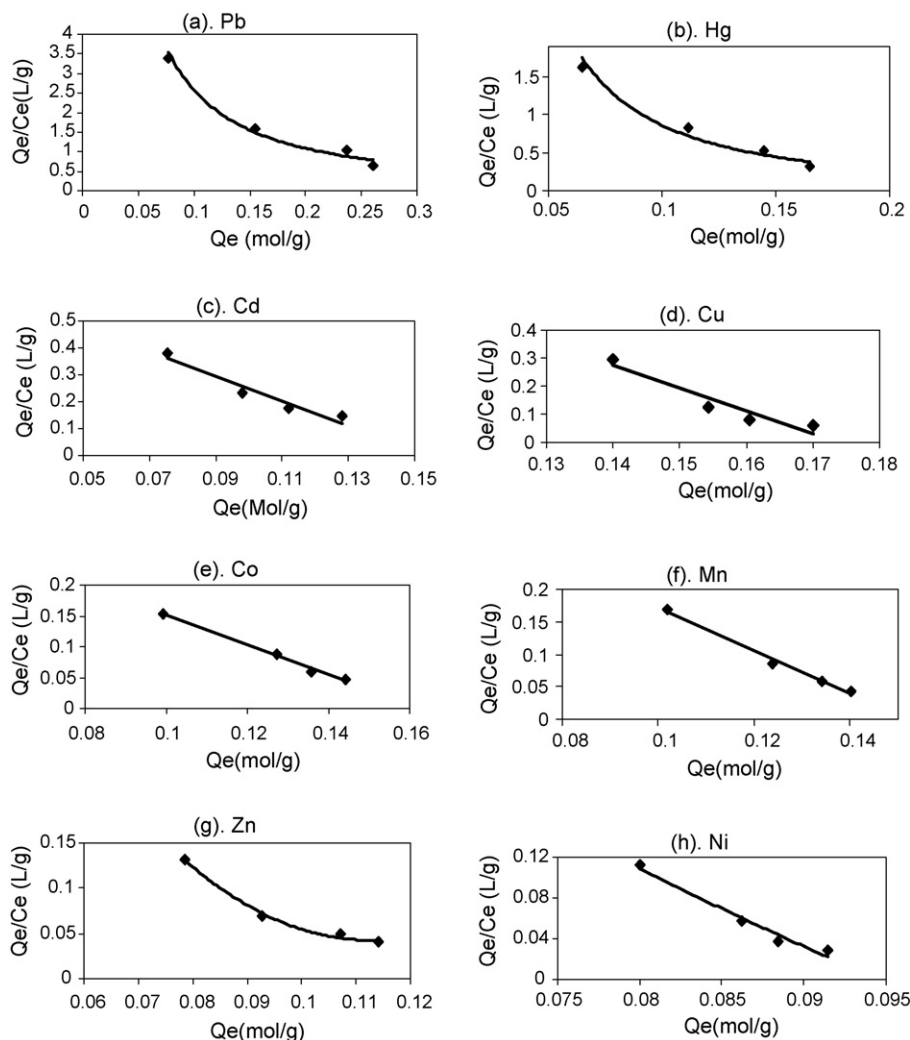
Fig. 5. Scatchard plots of metal ions on biomatrix.

order: $Pb^{2+} > Cu^{2+} > Ni^{2+}$. Gerente et al. [38] observed that the motions of Na^+ and K^+ ions are in the same order of magnitude and seem to be independent of the Cu^{2+} concentration, whereas, the release of number of moles of Ca^{2+} ions into solution was comparable with the fixation of Cu^{2+}, based on this they concluded that fixation is mainly due to ion exchange phenomenon between Cu^{2+} and Ca^{2+} and only 5% would be adsorbed. The role of Na^+ and K^+ ions on Cu^{2+} removal is low [38]. In the case of Pb^{2+}, Gerente et al. [38] observed an highest adsorption of 25% in the fixation among three metals used, whereas, Ni^{2+} seems to be fixed completely by ion exchange. These findings have been corroborated with the present research findings.

Sugar beet pulp, a common waste from the sugar refining industry was used for the removal of metal ions from aqueous solutions by Reddad et al. [19] and found that this has great potential for the removal of heavy metals from aqueous solutions with the affinity order: $Pb^{2+} > Cu^{2+} > Zn^{2+} > Cd^{2+} > Ni^{2+}$. They identified the predominant ion exchange mechanism involving numerous carboxylic groups of the galacturonic acid residues in the pectins. Lead presents great affinities for carboxylic moieties [41] found in *Penicillium chrysogenum* cell walls, mostly

composed of polysaccharides. Reddad et al. [19] suggested that probably other ligands are involved in the binding of Cd^{2+} to the biomass.

Dupont et al. [25] demonstrated the interest of natural organic matter in the retention of heavy metal ions and has extracted a lignocellulosic substrate from wheat bran, which is able to fix these three metal ions efficiently in the order: $H^+ \approx Cu^{2+} \approx Pb^{2+}$ and Cd^{2+} ions. Greater affinity of H^+ ions have also been observed by Ravat et al. [39] with a lignocellulosic substrate and it is classic in the case of humic substances [42,43].

3.6. Scatchard and Dahlquist interpretation of surface binding site heterogeneity

Scatchard [44] and Dahlquist [45] have proposed the following interpretation for binding site heterogeneity: if the straight line is obtained by plotting Q_e/C_e versus Q_e then the sorbent presents only one type of sites and a convex curvature indicates a single site binding with positive cooperativity and a concave curve shows the binding with a negative cooperativity phenomenon between strong and weak binding sites. In the
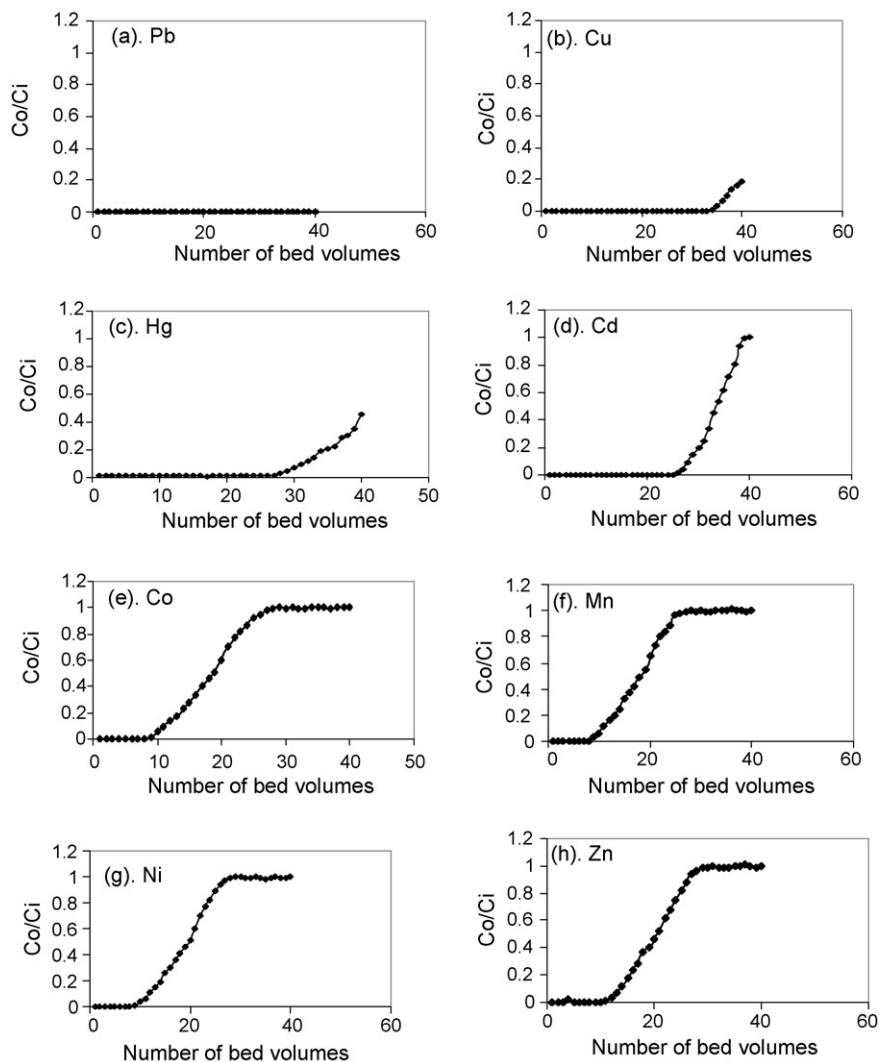
Fig. 6. Experimental breakthrough curve for adsorption of metal ions on biomatrix.

present study, straight lines (Fig. 5) were obtained for Ni^{2+}, Co^{2+}, Mn^{2+}, Cu^{2+} and Cd^{2+} which could prove an exclusive fixation by ion exchange on one site type, whereas for Pb^{2+}, Hg^{2+} and Zn^{2+}, the Scatchard plot presents concave curve (Fig. 5) which indicates the presence of two different types of site. Gerente et al. [38] have plotted these curves for Ni^{2+}, Cu^{2+} and Pb^{2+} at pH 4 and they found the straight line for Ni^{2+} and concave curve for Pb^{2+}; however, for Cu^{2+}, they found a convex curve, then a single site binding with positive cooperativity.

3.7. Column adsorption studies

The results obtained from batch adsorption experiments were used to remove metal ions by column. Experimental breakthrough curves for the metal ions adsorption on the biomatrix are shown in Fig. 6. As evident from the figure, there was no leakage of Pb^{2+} throughout the bed volumes with an initial concentration (C_i) of 12.5 mg/L. In the case of Cu^{2+}, Hg^{2+} and Cd^{2+}, there was no leakage up to 25–33 bed volumes with an initial concentration (C_i) of 12.5 mg/L, whereas in the case of

Ni^{2+}, Zn^{2+}, Mn^{2+} and Co^{2+}, there was no leakage up to 8–10 bed volumes. After these bed volumes, the column effluent concentration (C_0) increases gradually and attains the influent concentration at around 40 bed volumes. The biomatrix exhibits greater adsorption capacity due to higher initial concentration and optimum pH. The breakthrough curves were used to calculate the column capacity at complete exhaustion, which is greater than in the batch experiments. The flow rate was varied to achieve the maximum removal of the biomatrix and it was found that the maximum uptake of metal ions was achieved at flow rate 0.2 mL/min. About 65–100% of metal ions are removed at lower flow rates (0.2–1.0 mL/min), while this decreases with increased flow rate (1.0–2.0 mL/min). The higher column capacity may be due to the fact that a continuously large concentration gradient occurred at the interface as it passes through the column, while the concentration gradient decreased with time in the batch experiment.

Column flow experiment with multiple ions revealed the clear sorption preference for Pb^{2+} and Cu^{2+}. Similar results were found by Gerente et al. [37] on biosorption of Pb^{2+}, Cu^{2+} and

Ni^{2+} on sugar beet pulp and it was also reported that Ni^{2+} has very less competitive effect.

Fig. 7(a) represents the release of Ca^{2+}, Mg^{2+} and Na$^+$ with respect to bed volumes. From this it is evident that the unique ability of the biomatrix from rice husk to bind as many as eight metals can be attributed to the presence of sufficient Ca^{2+} and Mg^{2+} ions for ion exchange and functional groups which attract and sequester metal ions [35]. The release of Na$^+$ ions was in continuous decreasing order up to four bed volumes and thereafter there was no release, which indicates that initial release of Na$^+$ ions are in the same decreasing order of magnitude and seem to be independent of the metal ion concentrations.

3.8. Detoxification of hexavalent chromium

Studies conducted on the removal of Cr(VI) using biomatrix prepared from rice husk at pH 6 revealed that this species cannot be biosorbed by the biomatrix, because this exist as an oxo-anion, which cannot bind to the negatively charged carboxylate ligands prevailing at higher pHs [35]. Conversely, the biomatrix binds Cr(VI) at pH 2.0.

The effect of time on reduction of Cr(VI) in acidic media (pH 2) was investigated and is shown in Fig. 7(b), which indicates that the concentration of Cr(VI) decreased slowly and, simultaneously, Cr(III) appeared in the acidic solution, nearly 50% of maximum adsorption capacity of Cr(III) was reached within 24 h. The initial rapid adsorption gives way to a very slow rate of approach to the equilibrium and saturation is reached only
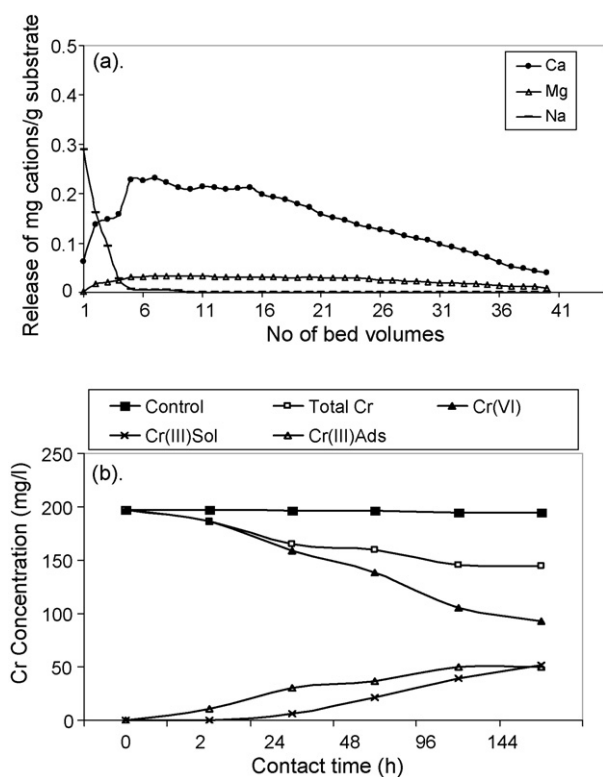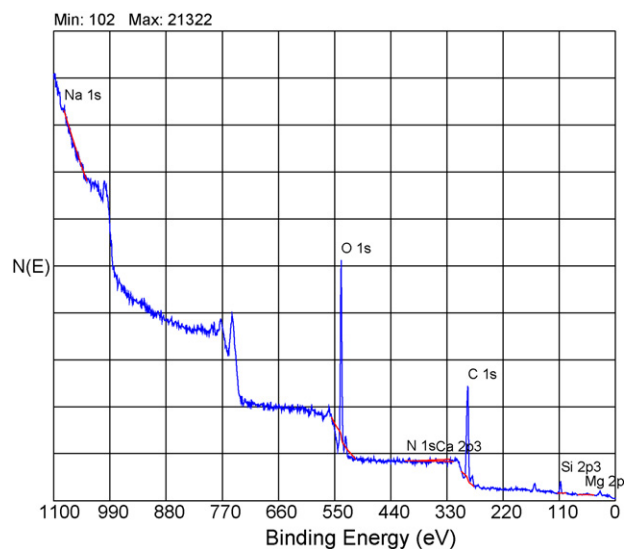

Fig. 8. XPS of biomatrix showing various elements.

after 96 h. Beyond 24 h, the concentration of trivalent chromium increases in the solution, which indicates that the removal of hexavalent chromium proceeds according to a redox process. Indeed, Cr(VI) in acidic solution demonstrates a very high positive redox potential [46], which denotes that it is strongly oxidizing and unstable in the presence of electron donors. In acidic solution, the HCrO$_4^-$ and Cr$_2$O$_7^{2-}$ ions are the predominant forms of Cr(VI). Reduction of these species is accompanied by the H$^+$ consumption [18,47] as follows:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- = 2Cr^{3+} + 7H_2O$$

$$HCrO_4^- + 7H^+ + 3e^- = Cr^{3+} + 4H_2O$$
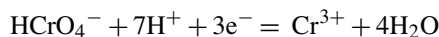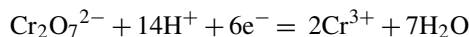
Carboxylic and hydroxyl groups present in the biomatrix probably play a role of electron donors. Biomatrix only facilitates electron transfer process, but does not undergo any change. The total chromium concentration was found to slightly decrease, thus the adsorption of chromium species also occurred with reduction of Cr(VI). Cr(III) was probably the chromium species effectively sorbed onto the biomatrix; however, Cr(VI) adsorption cannot be totally excluded. Studies conducted by Baig et al. [35] on the desorption of chromium revealed the complete recovery of Cr(III) from biomass and low recovery of Cr(VI) was due to the fact that it is reduced by the biomass to Cr(III) and is thus more strongly bound. Based on the studies conducted on the removal of Cr(III) and Cr(VI) from aqueous solutions using on sugar beet pulp as a biosorbent substrate under various experimental conditions, Reddad et al. [23] found that a part of the strong carboxylic groups play the electron donor role in the Cr(VI) reduction mechanism with the appearance of Cr(III) ions in the solution and about half of the carboxyl groups content was lost after 24 h contact time with Cr(VI) anions.

Dupont and Guillon [24] conducted studies on the adsorption isotherms with pure cellulose and pure lignin in acidic medium, and observed no significant sorption onto cellulose, whereas there was an extensive conversion of hexavalent Cr(VI) with lignin. These observations clearly demonstrate that the adsorp-

Fig. 7. Determination of removal mechanism: (a) release of cations (Ca^{2+}, Mg^{2+} and Na$^+$) from biomatrix in column adsorption experiment and (b) reduction of Cr(VI) using biomatrix at pH 2.
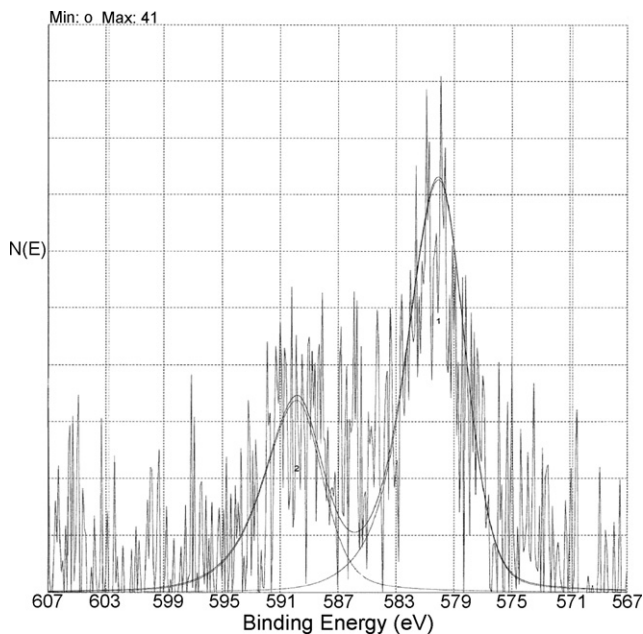
Fig. 9. XPS of chromium-loaded biomatrix.

tion reaction of Cr(VI) onto lignocellulosic substrate involves lignin moieties. In the present study, adsorption is greater at low pH and decreases with increasing pH, which can be attributed to the involvement of lignin in the reduction of hexavalent chromium into Cr(III) at low pH, and the subsequent adsorption of Cr(III) onto the adsorbent. The conversion of Cr(VI) mainly depends on the proton concentration. The higher the proton concentration, the higher the efficiency of Cr(VI) conversion. Such dependence was already observed with anionic materials [48]. It has been explained both by a surface exchange reaction between chromate and hydroxyl ions, which favors chromate adsorption in acidic media, and by the reduction process of hexavalent to trivalent chromium, which requires a large amount of protons.

Krishnani et al. [26] and Parimala et al. [27] have studied the efficacy of five different types of materials prepared from bagasse and coconut husk for detoxification of Cr(VI) from coastal waters. They found that acid-treated materials are the most effective materials for detoxification of Cr(VI) in the acidic medium, this can be attributed to the reduction of Cr(VI) into Cr(III), whereas the removal of Cr(VI) in the treatments with other materials prepared from bagasse and coconut husk in alkaline medium has been attributed to the reduction by increase in native microbial community in the coastal water.

3.9. X-ray photoelectron spectroscopy

Quantification of metals sorbed was possible only with the sample containing a high level of sorbed metal. However, this is very much useful in species identification and relative abundances. The XPS survey spectrum of lignocellulosic biomatrix consists of two major elements: carbon and oxygen and other elements are calcium, magnesium, sodium and silicon (Fig. 8). The presence of sorbed chromium has been detected on the biomatrix after chromium sorption, and the Cr 2p peaks have been analyzed

(Fig. 9). It consists of two contributions corresponding, respectively, to 2p$^{1/2}$ and 2p$^{3/2}$ energy levels. The XPS spectrum of chromium-treated biomatrix reveals an extensive reduction of Cr(VI) sorbed onto biomatrix to its trivalent form. Indeed, the two contributions of Cr 2p peaks of chromium sorbed are 576.3 and 587 eV, which compare well with the binding energies of Cr(III) in Cr$_2$O$_3$ at 576.3 and 586.2 eV reported by Boddu et al. [49]. These studies show that the lignocellulosic biomatrix is an efficient adsorbent for Cr(VI) removal from aqueous solutions, owing to its very low cost and its relatively interesting sorption capacity, which could be related to the abundance of lignin and fatty acid moieties, which allow the reduction of Cr(VI) into Cr(III) on carboxylic moieties. Previous literature [20] showed that Cr(VI) induces oxidation of only lignin components and that the retention of Cr ions occurs through a complexation reaction involving carboxylate moieties of lignin. The presence of sorbed cadmium and mercury have also been detected on lignocellulosics after cadmium and mercury sorption, and the 3d5 (406–410 and 413–417 eV) peak (Fig. 10) and 4f7 (103–110 eV) peak (Fig. 11) have been analyzed, respectively.

3.10. Fourier transform infrared spectrometry

FTIR technique is used mainly to identify functional groups (like carboxyl, hydroxyl, etc.) that are capable of adsorbing metal ions. The percentage transmission for various wave numbers and the absorption bands identified in the spectra of biomatrix are presented in Fig. 12. This reveals the presence of several functional groups for binding metal ions onto the biomatrix. Wave number of 3345.89 cm^{-1} indicates the presence of OH groups on the biomatrix surface. The 1647.88 cm^{-1} band is a result of C=O groups. The wave number observed at 1026.91 cm^{-1} is due to C–O group in carboxylic and alcoholic groups. The intensity is a function of the change in electric dipole moment and also the total number of such bonds in the sample. The band of C–O group
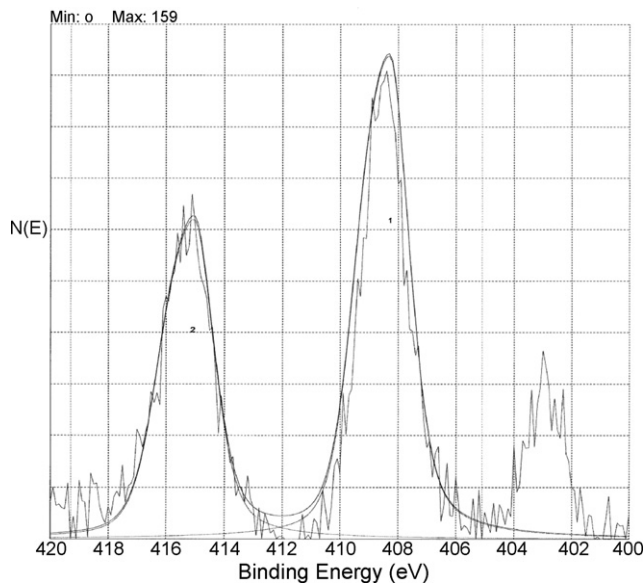

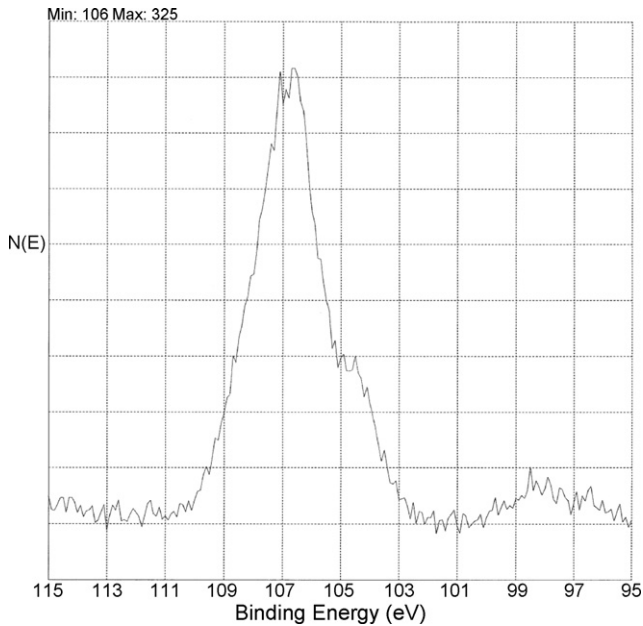Fig. 10. XPS of cadmium-loaded biomatrix.

Fig. 11. XPS of mercury-loaded biomatrix.

is more intense than that of C=O group, possibly because of more C−O groups present in the biomatrix. Ahalya et al. [13] used FTIR to determine the role of functional groups present in husk of Bengal gram (*Cicer arientinum*) in biosorption of Cr(VI).

3.11. Regeneration of metals

Regeneration and recovery of the column is an important aspect in wastewater treatment process and, therefore, desorption of lead and chromium was tried with a number of eluents by Gupta and Ali [12], they observed that the column can be used for at least 10 runs without any problem. In the present study, after the removal of metal ions from waters, bound metal ions were recovered by treatment with HCl or HNO$_3$. Regeneration, though technically feasible, there is no need to regenerate rice

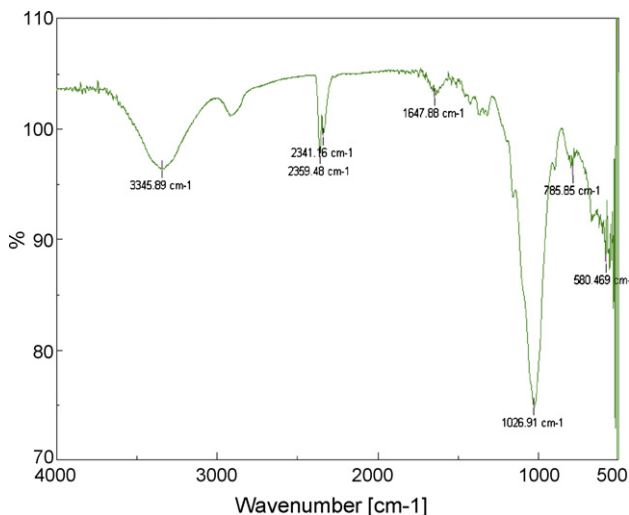Fig. 12. FTIR of biomatrix showing functional groups.

husk biomatrix as this lignocellulosic biomatrix is abundantly available inexpensive material.

4. Conclusions

Batch and column adsorption studies indicate that the newly developed biomatrix obtained by partial alkali digestion of rice husk could be used to remove as many as eight different metal ions (Ni, Zn, Cd, Mn, Co, Cu, Hg and Pb) in single and mixed metal solutions effectively. Adsorption follows both Langmuir and Freundlich isotherms, probably due to the real heterogeneous nature of the surface sites involved in the metal uptake. Studies revealed that biomatrix has sufficient calcium, magnesium and many −OH and −COOH groups in the linocellulosic moieties, which are the sites for ion exchange with metal cations. The chemical improvement by partial alkali digestion in autoclave has enhanced surface area and facilitation of transport of metal ions to the binding sites onto biomatrix. The biomatrix also reduces Cr(VI) to Cr(III) in acidic medium, wherein lignin and carboxylic functional moieties present in the biomatrix act as an electron donor. A comparison of the results of the present investigation with those reported in the literature showed that rice husk biomatrix is comparable with other adsorbents. However, due to very low cost of biomatrix, this might be an interesting material in the treatment of metal-contaminated water and represent an advantageous aspect when designing water treatment systems. Once the bound metal ions are recovered in acidic medium, biomatrix is biodegradable, and environment friendly.

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