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Use of chemical modification and spectroscopic techniques to determine the binding and coordination of gadolinium(III) and neodymium(III) ions by alfalfa biomass

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Abstract

Metal pollution in the aqueous environment has become an important issue in the past few decades leading to extensive research in the area of pollution remediation. Most of the recent research in this area has been in bioremediation including phytofiltration and phytoextraction. Although there has been a lot of research done in the field of metal interactions with plants, the actual mechanism(s) and ligands involved are not well understood. Through a series of batch experiments, including pH profiles, time dependency studies, and capacity experiments, we have investigated the binding of Gd(III) and Nd(III) to alfalfa biomass. Batch pH studies showed that the optimum binding was at pH 5.0 for both elements. The time dependency experiments showed that the binding occurs within the first 5 min of contact and remains constant for up to 60 min. In addition, chemical modifications to the alfalfa biomass were performed to indirectly determine the ligands on the biomass responsible for metal binding. For Gd(III) binding, it was shown that the carboxyl groups on the biomass play the most important role in metal ion binding. However, for Nd(III), not only was it found that the carboxyl groups play an important role in the binding, but in addition, the amino groups on the biomass also play an important role in the binding of the metal ions. Further studies using X-ray absorption spectroscopy (XAS) showed that the Gd(III) and Nd(III) ions were bound to the alfalfa biomass through oxygen (or nitrogen ligands), which were coordinated to carbon atoms. The lanthanide complexes within the biomass included some coordinated water molecules.

Keywords: Alfalfa; XAS; Lanthanides; ICP-OES

1. Introduction

The lanthanide elements are very unique to scientists because they possess some specific properties not exhibited by the other transition elements. For example, many of the lanthanide elements have high magnetic moments and superconducting properties. The high magnetic moments allow the lanthanide elements to be used in medical applications such as contrast agents for magnetic resonance imaging [1,2]. Studies have been performed which indicate that europium(III) compounds may have use in anti-cancer therapies [3,4]. Because uses for the lanthanide elements continue to be discovered and developed, there is an increasing need to develop new efficient ways to extract these elements from the environment, as mining stocks decline. Mineral stocks containing a high enough quality and quantity of these elements are hard to find even though the elements are quite ubiquitous in the natural environment at trace concentrations [5]. One such source for these elements may be their recovery from waste solutions, if a cost effective and efficient means of extracting these elements can be developed.

The pollution of natural waters with heavy metal ions has raised concern on how to remediate and clean waters. In addition, the dwindling mining stocks have also motivated research on how to inexpensively recycle metal waste, including metals in waste solutions [6]. In response to the pollution and remediation of natural waters and the need to develop a cheap and effective technology to extract heavy metals from

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water and waste solutions, many scientists have investigated the possibility of using natural products to remediate heavy metal contamination [7–18]. The binding of heavy metals to plants has been studied for almost two decades, and many different plant biomasses have been studied for their metal binding capabilities [7–18]. Plants such as alfalfa (*Medicago sativa*), creosote bush (*Larrea tridentata*), *Datura innoxia*, some algaes, and seaweeds are just a few of the plants that have been studied for the capabilities to bind heavy metals [19–23]. Many studies have been performed in an attempt to develop an effective and inexpensive method to remediate heavy metals from aqueous solutions. However, the plant–metal binding mechanism(s) are not well understood and researchers continue to use various techniques to try and comprehend the metal binding mechanisms and the ligands involved in the biosorption or phytofiltration of heavy metals.

Chemical modification techniques have been used to study the importance of particular functional groups in the binding of heavy metals to biomaterials. For example, chemical esterification of carboxyl groups was used to investigate the significance of carboxyl groups in the binding of copper(II), lead(II), and nickel(II) to different biomaterials [22,24–26]. Other chemical modifications used include ester group hydrolysis, sulfur group modification, and amino group modification. These modifications were done in order to study the effect of modifying the chemical functional groups on the binding of copper(II), cadmium(II), lead(II), europium(III), and gold(III) binding to biomaterials [27,28]. In addition, direct spectroscopic techniques have been used to investigate the chemical binding sites on or in biomaterials for heavy metals [29–31], and FTIR spectroscopy has been used to investigate the ligand coordinating different metals such as chromium(III) on or in biomaterials [31]. Solid state NMR and X-ray absorption spectroscopy (XAS) have been used to investigate the binding sites of europium(III), cadmium(II), copper(II), erbium(III), and holmium(III) binding sites in biomaterials [29,32]. XAS consists of two complimentary techniques, X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). The XAS technique is especially useful in the study of environmental systems because it provides very specific chemical information. XANES provides information on the coordination environment including atomic geometry (coordination), density of state, and the elemental oxidation state [29]. EXAFS provides similar information; however, it provides more specific parameters such as coordination numbers, the nearest neighboring atom(s), and the interatomic distances [29]. The combination of both of these techniques allows an understanding of the types of binding that are occurring within a sample and a better understanding of the chemical processes involved in the system under study. The usefulness of these techniques has been shown in the literature for the investigation on the structure of different lanthanide containing samples [33–40].

XAS provides structural information on compounds that are difficult to characterize crystallographically (e.g., amorphous materials) [29]. More specifically, Schlegel et al. [37] have used XAS to investigate Eu retention by calcium silicate hydrates, which showed that the Eu(III) ion replaces the calcium ion in the structure. In addition, XAS has been used to study the exchange kinetics of An(III) and Ln(III) in humate interaction [36]. Rocca et al. [35] have used XAS to study the coordination of Pr(III), Tb(III), and Er(III) in silica gels. A more classical example of the use of XAS to investigate lanthanide complexation involves studying the coordination and oxidation state of these ions within glasses [38–40]. Other investigators have used chemical modification and XAS studies to investigate the ligands involved in the sorption of gold(III), copper(II), chromium(III), erbium(III), and holmium(III) binding to alfalfa biomass [21,28,32,41]. The results of these studies have shown that the major ligands involved in the binding process, either directly or indirectly, of heavy metals to alfalfa biomass are carboxyl ligands on the biomass [21,28,32,41]. Kelley et al. used solid state NMR, FTIR, and XAS to elucidate the functional groups on water hyacinth responsible for europium(III) binding [30,42]. Carrilho et al. [43] used ^{113}Cd NMR and ^{27}Al NMR to show that the ligands involved in cadmium and aluminum binding to *Pilayella littoralis* contain oxygen, such as carboxyl groups, whereas Yun and co-workers [44] showed with FTIR spectroscopy that the functional groups responsible for metal binding on *Ecklonia* seaweed are carboxyl groups. Results from many studies show that the carboxyl groups in biomass play an important role in the binding of heavy metal ions from aqueous solutions. However, it is possible that there may still be other metal binding ligands contributing, either directly or indirectly, to the binding process.

In this study, various direct and indirect spectroscopic techniques were used to determine binding mechanism(s) and to identify the ligands involved in the phytofiltration of Gd(III) and Nd(III) ions from aqueous solutions. The indirect techniques used were biomass chemical modification and batch-type laboratory experiments such as pH profiles, time dependency experiments, and capacity experiments. There were five different chemical modifications performed on the alfalfa biomass within this study. The first modification was a chemical esterification performed to reduce the number of carboxyl groups, which are potential heavy metal binding sites on the biomass. The second and third modifications to the biomass blocked the amino groups, another possible heavy metal binding site on the biomass. The amino modification was performed in two different ways: the first involved the addition of an acetyl group to the biomass blocking the amino groups; the second modification involved the addition of a carboxylic acid function group to the biomass. The fourth chemical modification biomass was a hydrolysis, which was an attempt to increase the number of oxygen-bearing functional groups on the biomass to increase the total binding. The final chemical modification to the alfalfa biomass was the blocking of the sulfhydryl groups on the biomass.

By performing the chemical modifications to the alfalfa biomass and performing the different batch pH and capacity studies, an understanding of the importance of each of

the chemical functional groups to the sorption of Gd(III) and Nd(III) ions from aqueous solution can be developed. In addition, by studying the time dependency of the sorption to the native and chemically modified alfalfa biomass, an understanding of the type of reaction between the metal ions and the biomass can also be developed. Finally, the sorbent/metal reaction products were studied using XAS, a direct technique to determine which of the ligands on the sorbent were responsible for the metal ion sorption. In addition, the XAS will indicate if any metal ion reduction or oxidation is occurring, again helping to define the reaction mechanism.

2. Methodology

2.1. Reagents and solutions

All chemical reagents were of the highest purity. $Gd(NO_3)_3{\cdot}6H_2O$ and $Nd(NO_3)_3{\cdot}6H_2O$ were purchased from Strem Chemicals (Newburyport, MA). The chemical was 99.999% on the basis of Gd or Nd. All water used for solution preparation was deionized water. The nitric acid (Omni Trace pure HNO_3) and NaOH used in this study were purchased from Fisher Scientific (Pittsburgh, PA). All glassware was washed in 10% nitric acid and washed three times in deionized water before use. For the Gd solutions, a mass of 3.4327 g of $Gd(NO_3)_3{\cdot}6H_2O$ was weighed out and diluted to 0.1 L resulting in a 0.10 M solution. From this 0.10 M stock solution, further serial dilutions were made using acid-washed glass pipettes and volumetric flasks to make the appropriate solutions for all the studies performed in this investigation. The solutions containing Nd were made in a similar manner as the $Gd(NO_3)_3{\cdot}6H_2O$ solutions. A mass of 3.3026 g of $Nd(NO_3)_3{\cdot}6H_2O$ was diluted in 0.1 L of deionized water which resulted in a 0.1 M solution. Serial dilutions were performed using acid-washed glass pipettes and volumetric flasks to make the appropriate solutions for the studies performed in this investigation. The 1000-ppm solutions of Gd and Nd were made in HNO_3-washed glassware. Masses of 2.18 and 2.29 g of $Gd(NO_3)_3{\cdot}6H_2O$ and $Nd(NO_3)_3{\cdot}6H_2O$, respectively, were diluted in 1.0 L volumetric flasks. All solution concentrations were checked using ICP-OES with purchased analytical standards of the appropriate metal solutions.

2.2. Biomass collection

The alfalfa biomass was collected from controlled field studies located at New Mexico State University in Las Cruces, NM, USA. The alfalfa was washed and treated as previously published [27].

2.3. Biomass modification

Five different chemical modifications were performed on the biomass using previously published methods [25,27]. The first of the chemical modifications was an esterification, which involved reacting the biomass with an excess of acidified methanol to convert the carboxyl groups on the biomass in to their methyl esters [25]. The second biomass modification was a hydrolysis modification that involved reacting the biomass with 0.1 M sodium hydroxide, to increase the number of carboxyl and alcohol groups [25]. The third and fourth modifications were to the amino groups, and were performed in two ways: (a) the biomass was reacted with acetic anhydride, which adds an acetyl group to the biomass [27], and (b) the biomass was reacted with an excess of succinic anhydride, which adds an additional carboxyl group in the place of the amine group on the biomass [27]. Finally, the sulfur groups on the biomass were modified; this modification was performed by reacting the biomass with dithiopyridine, which converts the sulfhydryl groups to sulfur–sulfur double bonds [27]. The sulfhydryl groups on the biomass were also blocked by the addition of a pyridine group [27]. After chemical modification, all biomass samples were washed with deionized water, centrifuged, and lyophilized as previously published [27].

2.4. pH profiles

The pH profile studies were performed as previously published in the literature [6]. Separate 200 mg masses of sorbent, native and chemically modified alfalfa biomass, carboxyl resin, amino resin, and activated carbon were washed three times, once in dilute nitric acid (0.01 M HNO_3) and twice in deionized water to remove any soluble materials that may have interfered with the reactions. Each sorbent was centrifuged (Fisher Scientific 8K) at 3000 rpm for 5 min, and after each washing the supernatants were discarded. The sorbent was then resuspended in 40 mL of deionized water and then pH adjusted from pH 2 to 5, extracting triplicate 4.0 mL aliquots of the sorbent slurries at each pH. The pH adjusted sorbent was then centrifuged again at 3000 rpm for 5 min and the supernatants discarded. A 4.0 mL aliquot of 0.1 mM pH adjusted solution of either Gd(III) or Nd(III) was added to the pH adjusted sorbent. The sorbent/metal mixture was then equilibrated on a solution rocker for 1 h and subsequently centrifuged and the supernatants were stored for ICP-OES analysis. All ICP-OES analyses were performed using a Perkin-Elmer 4300 DV ICP-OES spectrometer and calibration curves with correlation coefficients of 0.99 or better were obtained for all analyses.

2.5. Time dependency studies

Time dependency studies were performed as previously published [6]. The sorbents were washed and pH adjusted to their optimum binding pH as mentioned in the pH profile section. The exception was the activated carbon and the amino resin. These were not studied due to their low percentage of adsorption and they were not a viable option for Gd(III) and Nd(III) ion recovery from aqueous solution. The sorbents were equilibrated on a rocker with 4.0 mL of a 0.1 mM so-

lution of either Gd(III) or Nd(III) for varying times of 5, 10, 15, 20, 30, and 60 min. After equilibration, the samples were centrifuged and the supernatants stored for ICP-OES analysis. All calibration curves obtained for the ICP-OES analyses had correlation coefficients of 0.99 or better.

2.6. Capacity studies

Capacity studies were performed as previously published [25]. The sorbents were prepared and washed as mentioned in the previous pH profile section. Again, the amino resin and the activated carbon were not studied due to their poor performance in the pH profile studies. The sorbents were then pH adjusted to the optimum binding pH of 5, as determined from the pH profiles. The sorbent was equilibrated on a rocker for 15 min with a 4.0 mL aliquot of a 0.3 mM solution of Gd(III) or Nd(III); the time was determined based on the minimum amount of time required for binding to reach a maximum, and centrifuged at 3000 rpm for 5 min and the supernatants stored for ICP-OES analysis. A fresh 4.0 mL aliquot of 0.30 mM of Gd(III) or Nd(III) was added to the reacted biomass and the equilibration was repeated. This equilibration and centrifugation process was repeated for 10 cycles or until the sorbent was loaded with the respective ions. All analyses were performed using ICP-OES and calibrations curves with correlation coefficients of 0.99 or better were obtained.

2.7. ICP-OES optimization and parameters

Different parameters on the ICP-OES spectrometer were studied in order to obtain the optimal ICP-OES parameters to study Gd and Nd. The flow rates of the samples were varied from 1.0 to 1.75 mL/min; the nebulization rate of the sample was also varied from 0.5 to 1.0 L/min. The torch power was varied from 1300 to 1500 W. The optimal operational parameters for the ICP-OES spectrometer are shown in Table 1.

2.8. XAS sample preparation and data collection

A mass of 500 mg of the native alfalfa biomass, chemically modified alfalfa biomass, and the carboxyl resin was weighed and washed three times. The washing stages consisted of one washing cycle in 50 mL of dilute nitric acid and two washing cycles in 50 mL of deionized water. Between each washing, the biomass was centrifuged at 3000 rpm for 5 min and the supernatant discarded. The sorbents were then resuspended in 40 mL of deionized water and pH adjusted to pH 5 or 2 using diluted solutions of sodium hydroxide and nitric acid; they were subsequently centrifuged. The supernatants were discarded and the sorbents were resuspended in 40 mL of a 1000-ppm solution of either Gd(III) or Nd(III), made from their respective nitrate salts. The sorbent/metal slurry was then equilibrated on a rocker for 1 h. After equilibration, the samples were centrifuged again at 3000 rpm for 5 min and the supernatants discarded. After centrifugation, the samples were washed using deionized water to remove any excess of unbound metal and the supernatants discarded again. The washed samples were then placed in liquid nitrogen for 45 min, and lyophilized in a Labconco freeze-dryer (Freezone 4.5) until dry. The lyophilized samples were then packed into 1.0 mm samples plates with Kapton® windows for analysis at the Stanford Synchrotron Radiation Laboratories (SSRL) in Palo Alto, CA, for XAS analysis [25,26,28].

Table 1
Optimized ICP-OES parameters for Gd and Nd determination

Parameter	Gd value	Nd value
Wavelength (nm)	342.27	406.109
Argon flow rate (L/min)	15	15
Auxiliary gas flow (L/min)	0.2	0.2
Nebulization rate (L/min)	0.65	0.65
Torch power (W)	1500	1500
View	Axial	Axial
Integration time (s)	10–20	10–20

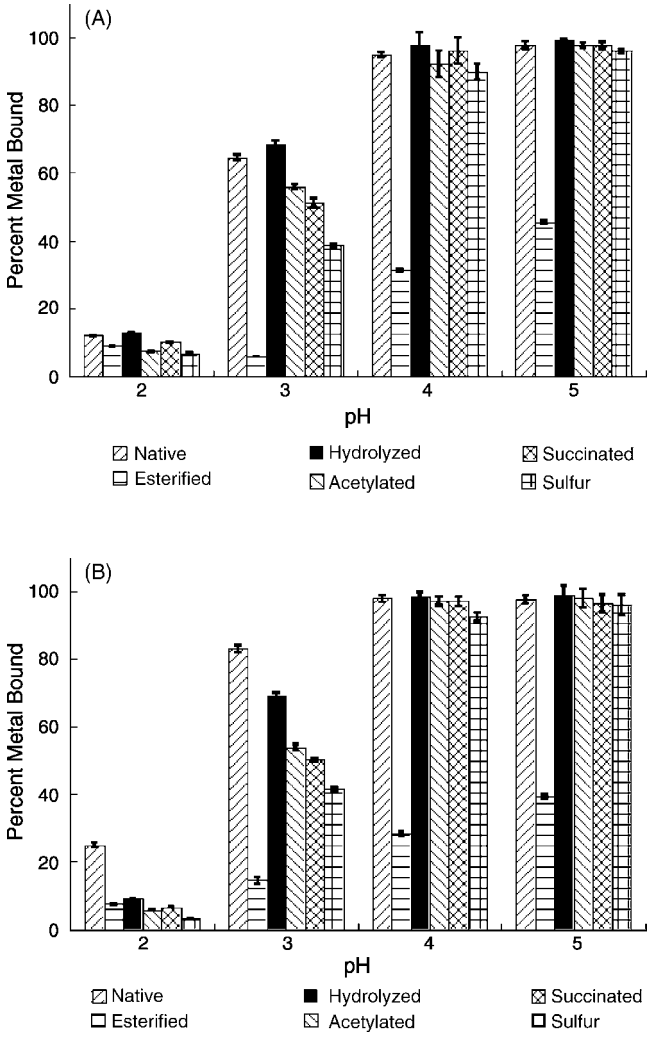

Fig. 1. (A) pH profile for gadolinium(III) binding to native and chemically modified alfalfa biomass. (B) pH profile for neodymium(III) binding to native and chemically modified alfalfa biomass.

All samples were run at SSRL on beam-line 2–3 using a liquid helium cryostat at approximately 10 K. The samples were analyzed in a liquid helium cryostat to reduce thermal disorder in the samples, which causes dampening of the signal as well as poor signal to noise ratios. The operating conditions of the beam-line included a double crystal Si(2 2 0) Ø 90 monochromator, a beam energy of 3 GeV, and a current of 60–100 mA. In addition, the samples were run in the transmission mode using ion chambers filled with nitrogen gas. The model compounds were diluted using boron nitride and analyzed in the same manner as the samples. The dilution procedure was to dilute the model compounds in boron nitride by grinding the model compounds in a mortar and pestle until a homogenous mixture was achieved, which gave a one absorption unit change across the absorption edge. The sample and model compounds spectra were collected on their respective L_{III} edges 6.208 and 7.243 keV for Nd and Gd, respectively [45]. For all sample data acquisitions, the beam-line was detuned by 50% to reject higher order harmonics that would make data analysis more difficult [26].

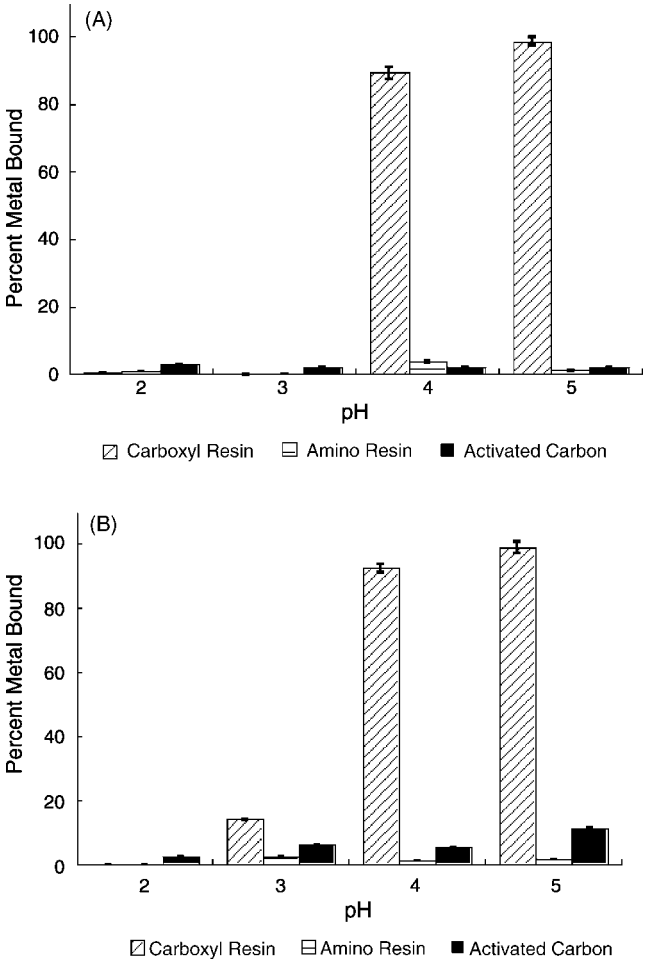

Fig. 2. (A) pH profile for gadolinium(III) binding to the amino resin, carboxyl resin, and activated carbon. (B) pH profile for neodymium(III) binding to amino resin, carboxyl resin, and activated carbon.

2.9. XAS data analysis

All XAS data analysis was performed using the WinXAS software and standard methods [46]. The spectra were first calibrated on the basis of the inflection point of the pure metal foil for Gd and Nd, respectively. The spectra were then background corrected using a two-polynomial fitting, a first-degree polynomial was used on the pre-edge region, and a third-degree polynomial fitting curve was used on the post-edge region and normalized to one absorption unit. The XANES spectra were then extracted from the entire spectra by sectioning the spectra from 7.2 to 7.3 keV and from 6.05 to 6.30 keV, for Gd and Nd spectra, respectively.

The EXAFS spectra were extracted from the XAS spectra by the following procedure: the background corrected spectra were converted into wave vector space (or k space or $Å^{-1}$). The conversion of the background spectra was performed on the basis of the energy of the photoelectron ejected from the

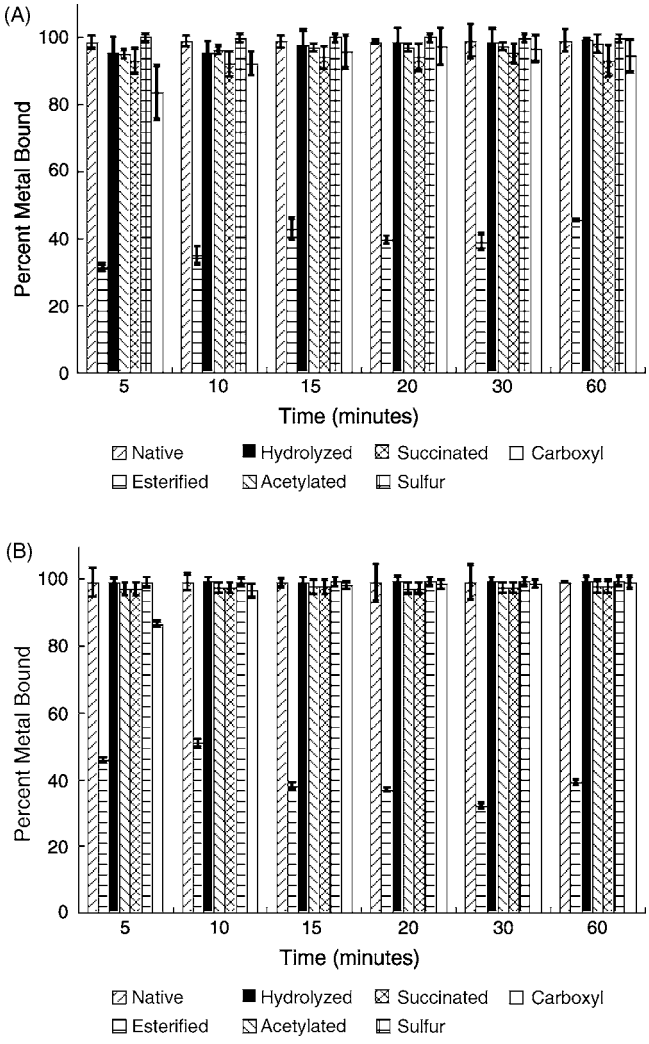

Fig. 3. (A) Time dependency studies of gadolinium(III) binding to native alfalfa biomass, chemically modified alfalfa biomass, and the carboxyl resin. (B) Time dependency studies of neodymium(III) binding to native alfalfa biomass, chemically modified alfalfa biomass, and the carboxyl resin.

Table 2
Binding capacities for Gd(III) and Nd(III) binding to the native alfalfa biomass, the chemically modified alfalfa biomass, and the carboxyl resin at pH 5.0

Sample	Capacity (mg/g)	C.I. 95%	Capacity (mmol/g)	C.I. 95%
Gd(III) native alfalfa	33.52	4.21	0.213	0.027
Gd(III) hydrolyzed alfalfa	82.47	14.39	0.524	0.092
Gd(III) esterified alfalfa	8.64	0.18	0.055	0.0012
Gd(III) succinated alfalfa	36.19	1.06	0.23	0.0068
Gd(III) acetylated alfalfa	36.64	1.73	0.23	0.010
Gd(III) sulfur-modified alfalfa	42.24	3.27	0.268	0.0208
Gd(III) carboxyl resin	93.75	2.16	0.596	0.014
Nd(III) native alfalfa	34.25	7.58	0.237	0.053
Nd(III) hydrolyzed alfalfa	41.57	1.84	0.288	0.012
Nd(III) esterified alfalfa	8.00	0.29	0.055	0.020
Nd(III) succinated alfalfa	19.14	0.99	0.133	0.0068
Nd(III) acetylated alfalfa	11.32	0.36	0.079	0.0025
Nd(III) sulfur-modified alfalfa	20.44	1.54	0.142	0.0108
Nd(III) carboxyl resin	42.85	0.63	0.297	0.0043

Note: C.I. 95% is the calculated 95% confidence interval.

absorption edge of the sample spectra. The sample spectra were then extracted using a spline of 7 knots and k weighted to 2. The sample spectra were then Fourier transformed from 2.0 to 11.2 $Å^{-1}$, and subsequently back transformed and fitted using FEFF V8.00 [47]. The inputs for the FEFF fittings were created using the ATOMS program [48]. The EXAFS were fitted using least squared fittings of the output from the FEFF program to calculate the interatomic distances, the

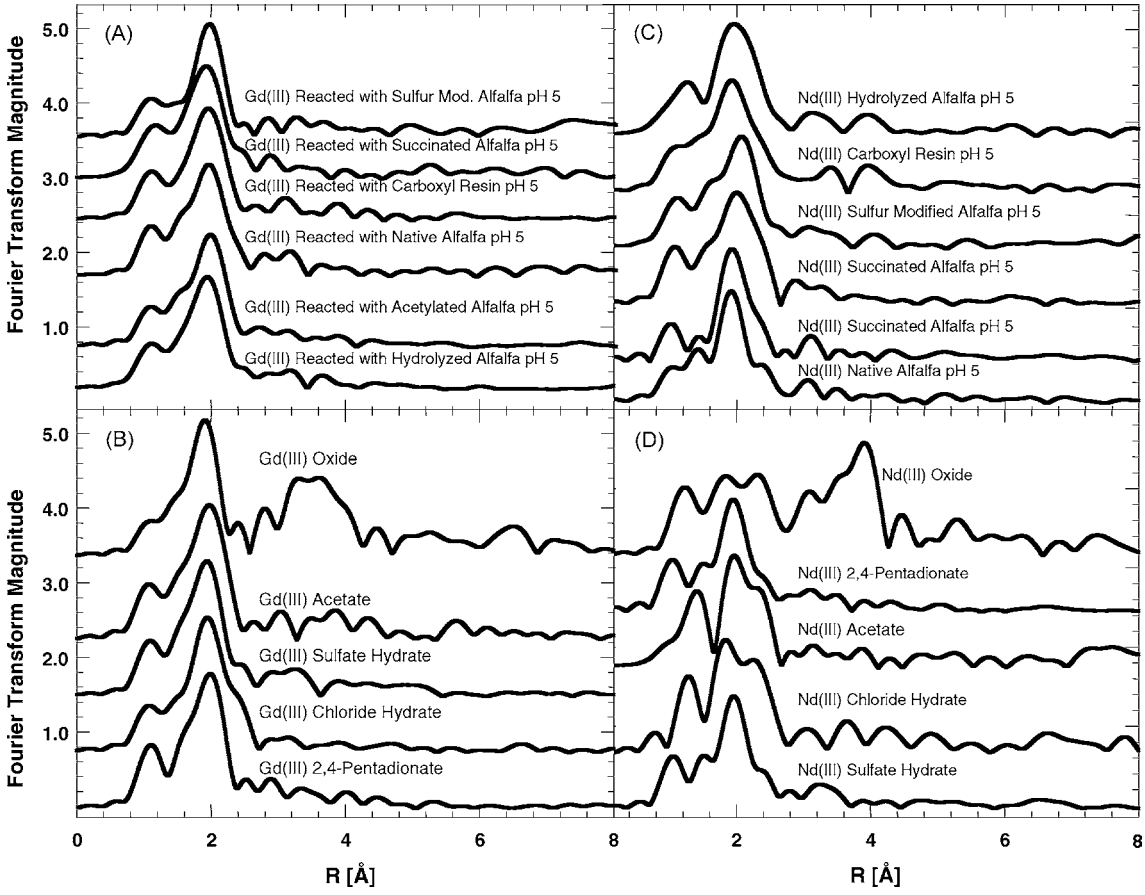

Fig. 4. (A) Fourier transformed Gd L_{III} EXAFS of gadolinium(III) binding to native alfalfa biomass, chemically modified alfalfa biomass, and the carboxyl resin (not phase and amplitude corrected). (B) Fourier transformed Gd L_{III} EXAFS of gadolinium(III) model compounds, gadolinium(III) acetate, gadolinium(III) 2,4-pentadionate, gadolinium(III) oxide, gadolinium(III) chloride hydrate, and gadolinium(III) sulfate hydrate (not phase and amplitude corrected). (C) Fourier transformed Nd L_{III} EXAFS of neodymium(III) binding to native alfalfa biomass, chemically modified alfalfa biomass, and the carboxyl resin (not phase and amplitude corrected). (D) Fourier transformed Nd L_{III} EXAFS of neodymium(III) model compounds, neodymium(III) acetate, neodymium(III) 2,4-pentadionate, neodymium(III) oxide, neodymium(III) chloride hydrate, and neodymium(III) sulfate hydrate (not phase and amplitude corrected).

number of neighboring atoms, the Debye–Waller factors, and energy shifts. The model compounds were fitted using the ideal crystallographic inputs from the literature and the unknowns were fitted using crystal structure of Gd(III) acetate and Nd(III) acetate.

3. Results and discussion

The results of the pH profile studies are shown in Figs. 1A and B and 2A and B, for Gd(III) and Nd(III) reacted with the native alfalfa biomass, chemically modified alfalfa biomass, and the ion-exchange resins, and activated carbon, respectively. The overall trend observed in the pH profiles for all adsorbents is a general increase in binding with an increase in pH, with the largest increase in binding occurring between pH 3 and 4. This trend has been observed for many different metals and sorbents; it also indirectly indicates that the functional group on the biomass responsible for the metal binding is the carboxyl group [49]. As seen in Fig. 1A and B, the chemical modification that had the largest effect on the sorption of the Gd(III) and Nd(III) ions from aqueous solution was the esterification. The esterification of the alfalfa biomass caused approximately a 60% decrease in the binding at the optimal binding pH of 5.0 compared to the other biomasses for both Gd(III) and Nd(III) ions. This strongly indicates that the carboxyl groups on the alfalfa biomass are responsible for the majority of the binding of the Gd(III) and Nd(III). In Fig. 2A and B, the amino resin and the activated carbon have less than 10% binding of the Gd(III) and Nd(III) ions from aqueous solution, indicating that the phenyl and the amino groups on the biomass are only minimally responsible for the binding of the metal ions. However, the binding trend observed for the carboxyl resin is very similar to that of the alfalfa biomass. A large increase in the percentage metal bound from solution is observed between pH 3 and 4, the range of the pK_a of the carboxyl groups on the resin and on the biomass. Similar behavior between the carboxyl resin and the biomass supports the idea that the major groups on the alfalfa biomass responsible for metal binding are the carboxyl groups.

Table 3
FEFF fittings of the gadolinium(III) reacted with native and chemically modified alfalfa at pH 5, and the fittings of the model compounds gadolinium(III) acetate, gadolinium(III) 2,4-pentadionate, gadolinium(III) oxide, gadolinium(III) chloride hydrate, and gadolinium(III) sulfate hydrate

Sample	Interaction	CN	R (Å)	σ^2 (Å^2)
Gd(III) reacted with native alfalfa, pH 5	Gd–O	3.0	2.31	0.0041
	Gd–O	6.4	2.45	0.0040
	Gd–C	4.6	3.60	0.0069
Gd(III) reacted with hydrolyzed alfalfa, pH 5	Gd–O	4.6	2.35	0.0017
	Gd–O	4.6	2.50	0.0016
	Gd–C	4.4	3.64	0.0022
Gd(III) reacted with succinated alfalfa, pH 5	Gd–O	4.0	2.34	0.0015
	Gd–O	4.5	2.51	0.0025
	Gd–C	2.9	3.47	0.0019
Gd(III) reacted with sulfur-modified alfalfa, pH 5	Gd–O	5.2	2.37	0.0025
	Gd–O	4.1	2.53	0.0047
	Gd–C	3.9	2.36	0.0043
Gd(III) reacted with carboxyl resin, pH 5	Gd–O	5.3	2.36	0.0039
	Gd–O	5.3	2.51	0.0052
	Gd–C	3.8	3.62	0.0039
Gd(III) reacted with acetylated alfalfa, pH 5	Gd–O	4.7	2.37	0.0010
	Gd–O	4.0	2.53	0.0019
	Gd–C	3.61	3.61	0.0016
Gd(III) acetate	Gd–O	3.4	2.38	0.0012
	Gd–O	3.9	2.54	0.0013
	Gd–C	3.1	3.61	0.0027
Gd(III) sulfate	Gd–O	2.8	2.25	0.0087
	Gd–O	7.2	2.40	0.0064
Gd_2O_3	Gd–O	1.6	2.13	0.0088
	Gd–O	6.7	2.32	0.0048
$GdCl_3{\cdot}6H_2O$	Gd–O	7.0	2.39	0.0054
	Gd–Cl	2.9	2.73	0.0078
Gd(III) 2,4-pentadionate	Gd–O	3.8	2.33	0.00053
	Gd–O	4.3	2.48	0.00081
	Gd–C	5.7	3.48	0.0061

Note: CN denotes the coordination number, R denotes the interatomic distances in Å, σ^2 is the Debye–Waller factor.

The results from the time dependency experiments are shown in Fig. 3A and B. As shown in this figure, the binding to all the studied sorbents occurs within the first 5 min of contact and remains constant up to 60 min. There is a slight observed decrease (approximately 10%) in binding with time of the Nd(III) on the esterified biomass. This could be a competition or a concentration effect; after the first 10 min of contact time, the biomass may have a higher concentration of Nd(III) than the solution and the concentrations may be equilibrating between the solution and the solid adsorbent. However, the other adsorbents and the lanthanide metals bound to the sorbents do not change with time, indicating that the binding is stable. Furthermore, the other biomass modifications do not cause the biomass to physically interact with the metal ions differently than the native alfalfa. This also indicates that the main groups on the alfalfa biomass responsible for binding of Gd(III) and Nd(III) ions are the carboxyl groups. If the binding was a complexation, a reduction in the oxidation state, or a ligand exchange reaction, then the kinetics of the reaction would be slower, as has been observed with the binding of gold(III) ions, platinum(II) and platinum(IV), and chromium(VI) to different adsorbents [6,28,50].

Table 2 displays the results of the capacity experiments for the native alfalfa biomass, chemically modified alfalfa biomass, and the carboxyl resin. Higher binding capacities were obtained for the Gd(III) binding to all the adsorbents studied. This difference in the binding capacities could be related to the ionic size of the Nd(III) and the Gd(III). The size of Nd(III) is approximately 0.04 Å, which could cause the metal ion not to fit correctly into the binding site on the different adsorbents. Additionally, it could be an indication of the presence of a secondary binding site on the alfalfa biomass for the binding of Gd(III) that becomes apparent through the chemical modification. There are also some differences in the chemistry between these two elements: Gd(III) forms daisy chain polymeric molecules whereas Nd(III) does not [5]. Other factors that may explain this binding difference could be binding affinity and equilibrium concentration during the reactions. That is, the sorbents may form a

Table 4
FEFF fittings of the gadolinium(III) reacted with native and chemically modified alfalfa at pH 5, and the fittings of the model compounds neodymium(III) acetate, neodymium(III) 2,4-pentadionate, neodymium(III) oxide, neodymium(III) chloride hydrate, and neodymium(III) sulfate hydrate

Sample	Interaction	CN	R (Å)	σ^2 (Å^2)
Nd(III) reacted with native alfalfa, pH 5	Nd–O	5.4	2.37	0.0033
	Nd–O	3.6	2.56	0.0062
	Nd–C	3.6	3.56	0.0013
Nd(III) reacted with hydrolyzed alfalfa, pH 5	Nd–O	5.4	2.38	0.0052
	Nd–O	6.4	2.56	0.0047
	Nd–C	4.8	3.71	0.0056
Nd(III) reacted with succinated alfalfa, pH 5	Nd–O	5.7	2.39	0.0026
	Nd–O	4.8	2.56	0.0026
	Nd–C	3.7	3.57	0.0028
Nd(III) reacted with sulfur-modified alfalfa, pH 5	Nd–O	3.6	2.29	0.0032
	Nd–O	6.6	2.49	0.0017
	Nd–C	3.0	3.58	0.0039
Nd(III) reacted with carboxyl resin, pH 5	Nd–O	4.9	2.36	0.0012
	Nd–O	4.9	2.53	0.0012
	Nd–C	4.4	3.8	0.0032
Nd(III) reacted with acetylated alfalfa, pH 5	Nd–O	4.9	2.35	0.0047
	Nd–O	6.0	2.54	0.0038
	Nd–C	2.3	3.53	0.0041
Nd(III) acetate	Nd–O	3.7	2.39	0.0016
	Nd–O	3.9	2.58	0.0012
	Nd–C	3.1	3.66	0.0089
Nd(III) sulfate	Nd–O	3.0	2.65	0.0021
	Nd–O	6.3	2.45	0.0029
Nd_2O_3	Nd–O	3.4	2.40	0.0086
	Nd–Nd	9.0	3.77	0.0081
$NdCl_3{\cdot}6H_2O$	Nd–O	4.6	2.38	0.0095
	Nd–Cl	2.9	2.79	0.0096
Nd(III) 2,4-pentadionate	Nd–O	3.3	2.54	0.0041
	Nd–O	6.0	2.37	0.0037
	Nd–C	4.6	3.56	0.0039

Note: CN denotes the coordination number, R denotes the interatomic distances in Å, σ^2 is the Debye–Waller factor.

weaker bond to the Nd(III) and as the concentration of the metal ion on the biomass increases above the solution concentration, the metal may be released from the biomass to the solution. This could explain the higher binding capacities observed for the Gd(III) ions over the Nd(III) ions. Table 2 shows that there is a general trend for higher binding capacities for the Nd(III) with the native alfalfa biomass, hydrolyzed alfalfa biomass, and the carboxyl resins. However, succination and acetylation result in a drastic decrease in the binding of the metal ions from solution. The succinated alfalfa biomass binds a higher amount than the acetylated alfalfa biomass, showing the importance of the amino group in the binding of the Nd(III) ions from aqueous solution. This is also shown in the pH profiles for the resins, where the Nd(III) reacted with the amino resin at pH 5 bound approximately 10% and the Gd(III) reacted with the amino resin bound only 2–3% of the Gd(III) ions from solution. In addition, the acetylated alfalfa biomass bound approximately 60% of the amount of Nd(III) compared to the succinated alfalfa biomass, showing the importance of the carboxyl group in binding Nd(III) from solution. However, the esterification of the alfalfa biomass almost eliminated the binding of both ions from solution, again showing the importance of the carboxyl group in binding both Gd(III) and Nd(III) ions from aqueous solution. Similar binding capacities have been shown for Gd(III) binding to *B. subtilis* from aqueous solution [51].

The results of the XAS studies are shown in Figs. 4A–D, 5A–C, and 6A–C and in Tables 3 and 4. Fig. 4A and B shows the Fourier transformed EXAFS spectra of the Gd(III) reacted with the different adsorbents and the Gd(III) model compounds. It should be mentioned that for the pH 2 reactions, the signal to noise ratios were too low to obtain useful EXAFS spectra for fitting purposes. As observed in Fig. 4A, the spectra of the Gd(III) bound to the different sorbents all appear to be very similar and they also appear to be the same as the Gd(III) acetate and Gd(III) 2,4-pentadionate. The Fourier transformed spectra of the samples have very similar features and peak shapes compared to the organic ligand model compounds. The FEFF fittings of the Gd(III) samples and model compounds are presented in Table 3. As seen in Table 3, the samples are coordinated to between eight and nine oxygen atoms, and on average, they have four and five oxygen atoms. The fittings indicate that at least three to four of the oxygen atoms are water molecules, indicated by the shorter interatomic distances of approximately at 2.3–2.4 Å, and the remaining oxygen ligands in the complex are from the biomass, at an approximate interatomic bond distance of 2.5 Å, which are coordinated to carbon atoms.

Similar results are seen for the Nd(III) reacted with the different sorbents, where there are approximately 8–10 oxygen atoms bound to the Nd(III) atom, split between two different shells, at approximately 2.3 and 2.5 Å. In addition, there is a third shell of atoms, which consists of approximately three to four carbon atoms at 3.6 Å. These types of coordination complexes have been observed for these elements in other systems in the literature, indicating coordination to the solid adsorbent and water molecules completing the coordination sphere [5]. The coordination observed in the samples very closely resembled a mixture of particular metal acetate and the 2,4-pentadionate as can be seen from the coordination numbers and interatomic distances given in Tables 3 and 4. Similar coordination complexes, with acetate type structures, have been seen with

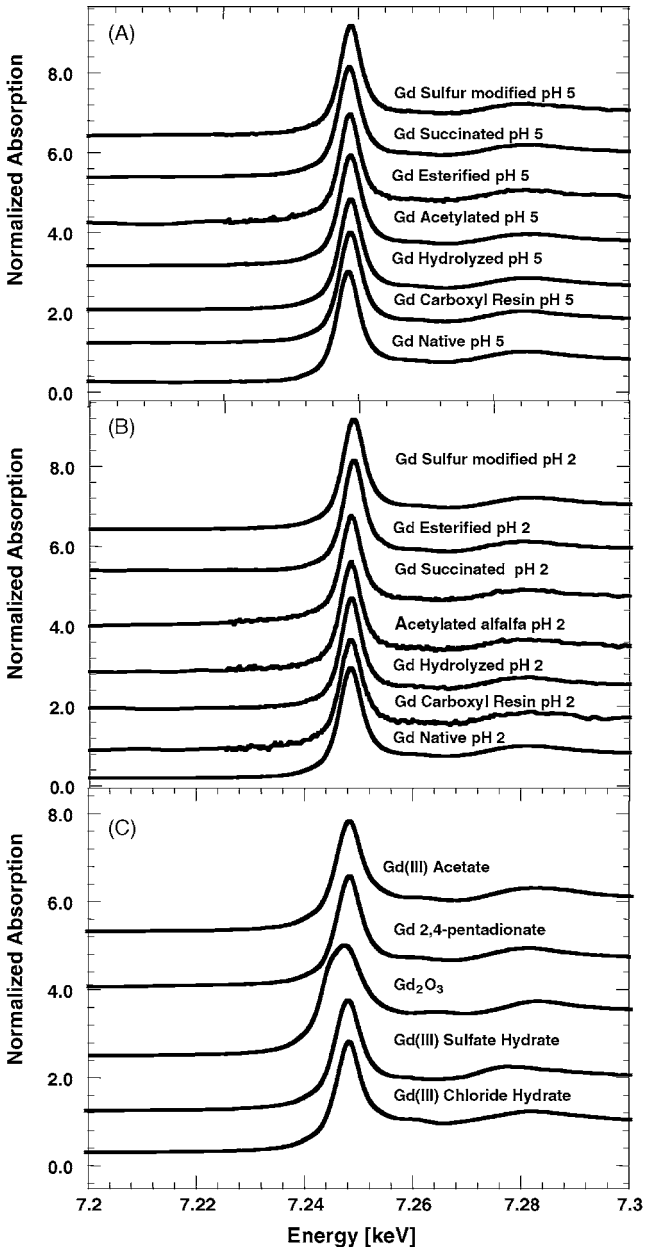

Fig. 5. (A) Gd L_{III} XANES spectra of the gadolinium(III) reacted with the native alfalfa biomass, chemically modified alfalfa biomass, and carboxyl resins at pH 5. (B) Gd L_{III} XANES spectra of the gadolinium(III) reacted with the native alfalfa biomass, chemically modified alfalfa biomass, and carboxyl resins at pH 2. (C) Gd L_{III} XANES of gadolinium(III) model compounds, gadolinium(III) acetate, gadolinium(III) 2,4-pentadionate, gadolinium(III) oxide, gadolinium(III) chloride hydrate, and gadolinium(III) sulfate hydrate.

other trivalent transition metal complexes with biosorbents [52].

The XANES spectra for the reactions of the Gd(III) and Nd(III) ions with adsorbents and model compounds are shown in Figs. 5 and 6, respectively. The XANES spectra provide information on the geometry of ligands attached to a compound and thus indicate if the reaction products are the same or different [53]. The geometry of a compound is determined through changes in the XANES spectra such as changes in the pre-edge features or changes in the shoulder region after the absorption edge can be observed. In addition, shifts in the positions of shoulders and the white lines also indicate changes in the geometry. The XANES region consists of the region approximately 20 eV before the inflection point of the absorption edge to approximately 50 eV past the absorption edge [53]. Fig. 5A–C shows the XANES of the reaction of the Gd(III) with the sorbents at pH 5, the XANES of the reaction of the Gd(III) with the different sorbents at pH 2, and the XANES of the model compounds. The XANES of the Gd(III) reacted with the sorbents at pH 2 and 5 all appear to be very similar and are similar to three model compounds Gd(III) 2,4-pentadionate, Gd(III) sulfate hydrate, and the Gd(III) acetate. The Gd(III) oxide and Gd(III) chloride have extra features present in the XANES region that make them appear different. The different geometrical arrangements of the atoms around the Gd(III) ion in different compounds make the XANES region appear different, which is shown in the XANES spectra of the model compounds. The position and the sharpness of the white line feature in the XANES spectra are different for the different geometrical arrangements. In addition, the position of the shoulder after the white line in XANES region appears at higher energy for the Gd(III) chloride and the Gd(III) oxide compared to the other model compounds and samples. As with the XANES of the Gd(III) samples, the XANES of the Nd(III) samples also appear to be similar to the acetate and the 2,4-pentadionate which all have coordination numbers of 9 giving them a complex geometry [5]. The XANES data compliment the EXAFS data showing that both Gd(III) and Nd(III) are bound to oxygen ligands on the alfalfa biomass with the presence of carbon in the outer shell.

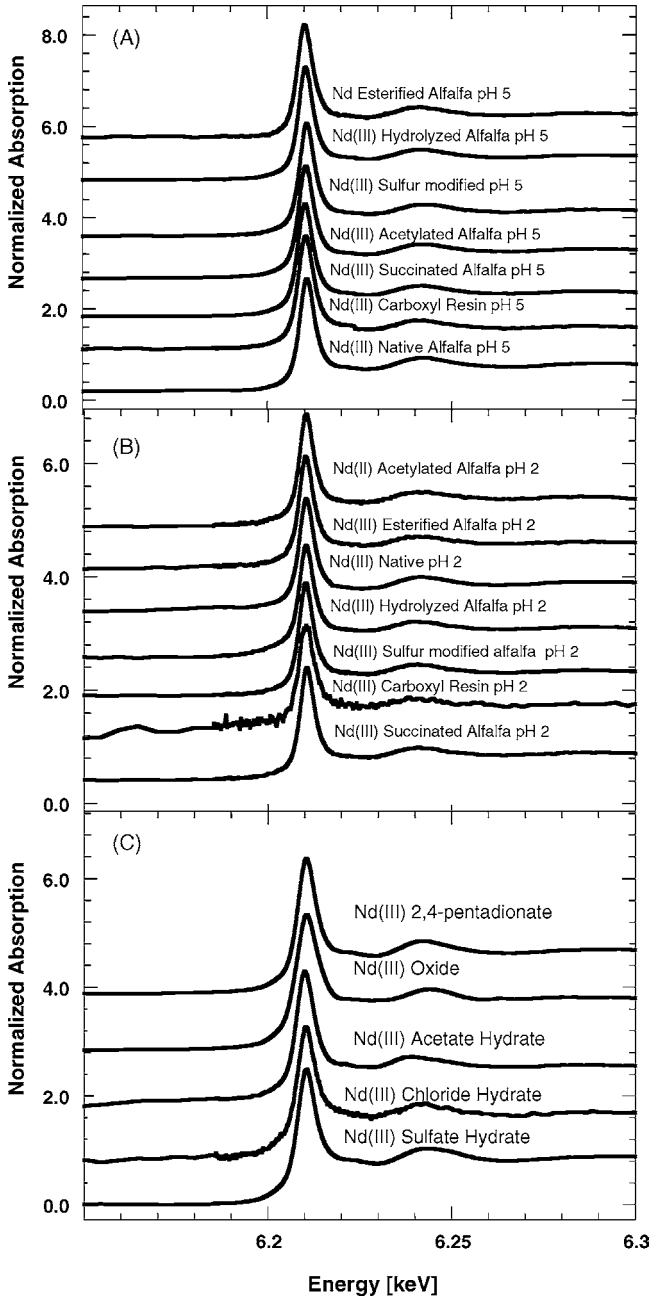

Fig. 6. (A) Nd L_{III} XANES spectra of the neodymium(III) reacted with the native alfalfa biomass, chemically modified alfalfa biomass, and carboxyl resins at pH 5. (B) Nd L_{III} XANES spectra of the neodymium(III) reacted with the native alfalfa biomass, chemically modified alfalfa biomass, and carboxyl resins at pH 2. (C) Nd L_{III} XANES of neodymium(III) model compounds holmium(III) acetate, neodymium(III) 2,4-pentadionate, neodymium(III) oxide, neodymium(III) chloride hydrate, and neodymium(III) sulfate hydrate.

4. Conclusions

The results from all the studies conducted show that the carboxyl groups play a vitally important role in the binding of Gd(III) and Nd(III) to alfalfa biomass. The results also show that alfalfa is a potential biosorbent for the recovery of Gd(III) and Nd(III) from aqueous solutions. In addition, the time dependency experiments showed that the biomass binds both Gd(III) and Nd(III) quickly and effectively from solution, showing almost 100% binding within the first 5 min of contact. The results of the pH profiles of the native alfalfa biomass, the chemically modified alfalfa biomass, and ion-exchange resins indicate that the carboxyl groups are the major functional group on the biomass responsible for the sorption of Gd(III) and Nd(III) to the alfalfa biomass. In addition, the capacity experiments show the importance of the carboxyl groups on the biomass for the binding of the studied metals as the esterification of

the alfalfa biomass almost eliminated the binding. However, the results on the binding of Nd(III) suggest that there is a secondary binding site which likely is an amino group on the biomass. Finally, the EXAFS and the XANES studies showed that both Gd(III) and Nd(III) binding to the alfalfa biomass occur through an oxygen ligand with an atomic geometry very similar to that of their respective acetates or 2,4-pentadionates.

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