

Retention of cobalt on a humin derived from brown coal

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Abstract

In this work, the retention of cobalt on a humin (HU) derived from a brown coal is studied. Through a systematic and coordinated investigation of the behavior of the metal ions in solution (speciation diagrams as a function of pH) and their adsorption and precipitation processes with reactive functional groups of the solid (sorption isotherms), the interactions of different Co(II) species with HU are probed. To further confirm the nature of these interactions, the complementary spectroscopic techniques of FTIR, Raman microspectroscopy, UV–visible absorption and XRD are employed. Molecular modeling techniques are used to gain information about the stability of different Co(II) species as a function of pH, as well as the stability of Co(II) species complexed with benzoic acid, a common surface component of humic substances. It is found that the selectivity that humin has for different Co(II) species, as well as the amount of Co(II) that it can retain, are both highly dependent on pH. Through Raman microspectroscopy measurements, the presence and location of Co(OH)₂ precipitates on the surface of HU is confirmed.

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1. Introduction

Humic substances (HS) can be properly viewed as highly functionalized, carbon-rich colloidal biopolymers with significant capacity for binding metallic cations. Major functional groups present in these materials are carboxylic acids and phenolic hydroxyls, but minor amounts of other groups, such as ketones, amines and thiols, are also always present [1]. Transition metals have many industrial applications and they are present in high concentrations in waste effluents of metallurgical, painting and extractive mining industries [2]. The interactions of humic substances with metals play an important role in their mobility and bioavailability in the environment [3] and, importantly, can be used to provide new environmentally friendly metal adsorbents. However, the partial solubility of some of its fractions (fulvic and humic acids) put HS at a disadvantage compared to other adsorbent materials (activated carbons, clays or zeolites), as the soluble humic macromolecules can stabilize metallic cations in solution [4–6]. In order to overcome this shortcoming, some efforts have been made. Ferro-

Garcia et al. [7] adsorbed soluble HS onto an activated carbon in the development of a system for the removal of Cr(III) cations from water; de la Rosa et al. [8] immobilized soluble HS on a silica matrix and employed the composite material as an adsorbent for the removal of different metallic ions; Helal et al. [9] extracted the insoluble fraction of a HS from the organic matter of a soil and used it as a high performance adsorbent for Cs⁺, Sr²⁺ and Gd³⁺ ions. However, it has been shown that the adsorption of HS onto insoluble substrates [10,11], and the extraction of humin from soils [1,12], are both laborious methods that can significantly increase the cost of fabrication of industrial adsorbents.

HS occur not only in soils, natural waters, rivers, lakes, sea sediment plants, peat and other chemically and biologically transformed materials, but also in lignite and oxidized bituminous coal [1,13–15]. The aim of this paper is to study the retention phenomena of cobalt ions on a brown coal derived humin (HU). The interactions between different species of Co(II) and HU can be deduced from the systematic and coordinated study of the behavior of the metal ions in solution (speciation diagrams as a function of pH) and the adsorption and precipitation processes of the metal ion with the reactive functional groups of the solid (sorption isotherms). Sorption isotherm analysis requires that experimental data be fit to a mathematical model. In the

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literature, there are several equations of diverse nature that have been used to fit sorption isotherms [3,16]. In previous papers [17–19], it has been verified that it is possible to fit sorption isotherm data to a model that postulates the existence of a certain singular global process that may be composed of one or more single adsorption processes.

Sorption isotherm analyses have permitted the acquisition of macroscopic information pertaining to sorption processes [16]. However, the hypotheses established in the interpretation of the isotherms require additional spectroscopic confirmation to be meaningful [20,21]. For this reason, FTIR [22], Raman microspectroscopy [23] and XRD [24] have been employed to determine the specific interactions of Co(II) species with the surface functional groups of HU. These techniques are of particular value as they provide information about changes in the surface functional groups of HU and the formation of possible crystalline phases on its surface. In addition, molecular modeling techniques have been employed to gain information about the stability of different Co(II) species as a function of pH [25], and the stability of Co(II) species complexed with benzoic acid, which is a common reactive surface component of humic substances.

2. Materials and methods

2.1. Humic samples

The adsorbent used in this work is a HU fractioned from a commercial HS supplied by Fluka, in accordance with the standards of the International Humic Substance Society [12]. The origin of this humic substance is brown coal from Northern Bohemia, produced by alkaline extraction of the coal, followed by acidification with hydrochloric acid solution (pH ~ 1), and washed several times with water. HU characterization included obtaining the chemical composition using a Carlo Erba EA 1108 elemental analyzer, and obtaining the porous texture by N₂ (77 K) and CO₂ (273 K) adsorption measured with a Micromeritics 2010 by the static volumetric method [26]. The quantity of strong acidic groups, and the total acidity of HU were determined by calcium acetate and barium hydroxide methods [1], respectively. The quantity of weak acidic groups was calculated as the difference between the total acidity and the number of strong acidic groups. The acid–base constants were estimated from the end points obtained from a potentiometric acid–base titration using a Metrohm Titrino 702SM autoburette. For the study of zeta potential (ζ) as a function of pH, a suspension containing 0.1 ± 0.0005 g of HU per liter of MilliQ-distilled water was prepared. The suspension was sonicated for 30 min, and aliquots of 50 ml were adjusted to the desired pH values by addition of 0.10 M HCl or NaOH. Different dispersions were placed in a thermostated water bath (Grant OPLS 200) at 298 K for 24 h, and pH was adjusted again. Zeta potential with pH was studied with a Zetasizer 3000HS (Malvern Instruments). Electrophoretic mobility was determined by injecting 15 ml of sample into a 5 cm pathlength—quartz cell, and applying a voltage of 120 V [27], and is related to ζ through Henry's equation [28].

2.2. Adsorption isotherms

Batch adsorption was carried out using scaled 50 cm³ centrifuge tubes made out of low-density polyethylene. Samples of HU (0.2500 ± 0.0005 g) were suspended in 20 cm³ of MilliQ-distilled water. The pH was adjusted with the addition of dilute HCl or NaOH solutions. Suspensions were then placed in a thermostated water bath (Grant OPLS 200) at 298.0 ± 0.2 K for 24 h. In order to obtain the complete sorption isotherms and so to study the maximum retention capacity varying amounts of cobalt (0, 10, 20, 40, 80, 120, 160, 320, 640 and 1280 mmol of Co(II) per kg of HU) were added to samples from a 10,000 ppm solution of CoCl₂·6H₂O (Merck, analytical grade), with its ionic strength adjusted to 0.05 mol dm³ using a 0.25 mol dm³ NaCl solution. The volume was then set to 25 cm³ and the pH was readjusted. Samples were then placed in the thermostated water bath for 24 h, centrifuged for 30 min at $14,000 \times g$ (Sigma, Mod. 2-16), and filtered (Millipore, 0.45 μ m). The Co(II) concentrations in filtrates were determined by AAS (Perkin-Elmer, Mod. 2100), and the amount of Co(II) retained was calculated as the difference between the initial and equilibrium amounts. The residue was vacuum dried at 333 K. The isotherm at pH 2 was replicated five times to test the reproducibility of adsorption data, and in all cases the percentage error was less than 1.9%.

2.3. Spectroscopic characterization

Supernatants having an initial concentration of 1280 mmol of Co(II) per kg of HU were analyzed by means of UV–visible spectrophotometry (Lambda 3B, Perkin-Elmer) to gain information about the principal species in solution. Selected isotherm samples (doped with 0, 80 and 1280 mmol of Co(II) per kg of HU), washed three times with ethanol for 5 min periods, vacuum filtered and vacuum dried at 333 K for 24 h, were characterized using transmission FTIR (Nicolet, Avatar 360) in pressed KBr pellets (150 mg KBr and 1 mg of sample). To remove atmospheric water vapor and CO₂ from the spectrophotometer, the transmission FTIR cell was flushed with N₂ gas for 10 min before scanning. The spectral resolution was set to 1 cm⁻¹ and 150 scans were collected for each spectrum. XRD (Siemens, D500) was recorded for the samples where FTIR showed the existence of a cobalt inorganic phase. Raman scattering experiments were conducted using a micro-Raman Renishaw InVia system with a Peltier cooled CCD detector, a Leica microscope and laser excitation at 633 nm (HeNe). All measurements were made in a backscattering geometry using a 50 \times microscope objective (Leica) with a NA value of 0.75, providing a scattering area of $\sim 1 \mu$ m². Spectra were collected in Renishaw's continuous collection mode with accumulation times of 10 s and 20 spectra being co-added in each experiment.

2.4. Molecular modeling

Semi-empirical calculations were carried out with HyperChem 7 [29] using ZINDO/1 methods. In accordance with the approach proposed by Starev and Zerner [30], unrestricted shell self-consistent field calculations were employed.

3. Results and discussion

The contents of C (39.8%), H (5.02%), N (0.21%), S (1.12%) and ash (16.4%) for this HU are quite in line with what is expected for materials of this type [1]. This is also true of its pK_a values (4.02 and 8.35), and the concentration of its acidic groups (2.12 and 2.46 mol kg⁻¹, for strong and weak acidic groups, respectively) [1,31]. The porous texture of this HU has been studied using adsorption isotherms of N₂ (77 K) and CO₂ (273 K). These adsorbates have similar molecular sizes (0.30 and 0.33 nm, respectively), but the sample adsorbed and retained CO₂ ($A_s = 53.7$ m² g⁻¹) and not N₂ ($A_s < 1$ m² g⁻¹). This can be explained by the extremely narrow microporosity of this material. Whereas CO₂ can penetrate into the micropores of HU, N₂ cannot, due to diffusion restrictions resulting from its lower kinetic energy at 77 K [28,32,33]. Zeta potential as a function of pH, are shown in Fig. 1. It can be seen that ζ values become more negative as pH is increased. A plot of ζ against pH shows drops in ζ values in the pH intervals 3.1–4.4, and 6.2–9.0, with a section of null slope between the two. The first of these drops is coincident with the equivalence point assigned to carboxylic acid groups, whereas the second one likely corresponds to the beginning of the ionization of the phenolic acid groups. The null slope section between these drops seems to indicate that the electrokinetic properties of the colloids do not change in this interval of pH values. From pH 6.2 upwards, ζ values decrease progressively due to gradual ionization of phenolic groups.

Fig. 2 shows the sorption isotherms of Co(II) on HU at constant pH, 298 K, and an ionic strength of 0.05 mol dm³ in NaCl. The amount of Co(II) retained, and the shape of the isotherms, both vary with pH. According to the criteria of Giles et al. [34,35], all of the sorption isotherms for HU can be classified as L-type. The sorption isotherms at pH values of 2.02 and 5.94 can be classified as L-1 type, while at pH 7.95 the isotherm can be classified as L-3 type. This variation of isotherm shape with pH is indicative of changes in the mechanisms of metal retention on HU [19]. L-type isotherms are characterized by initially high slope values that decrease as equilibrium metal ion concentra-

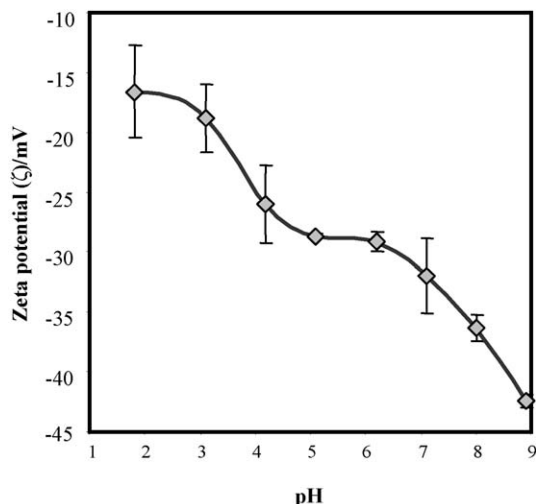


Fig. 1. Zeta potential of HU as a function of pH.

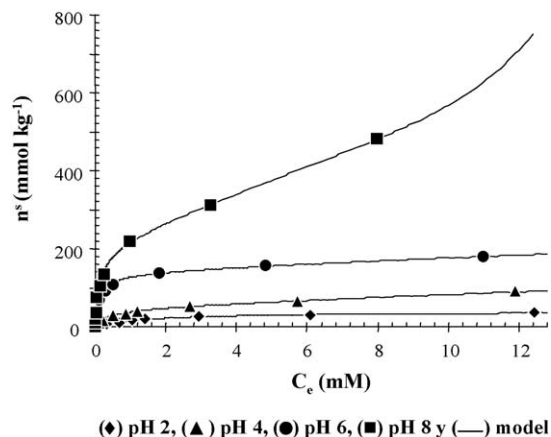
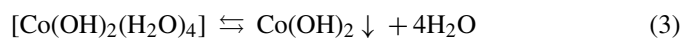
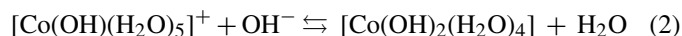
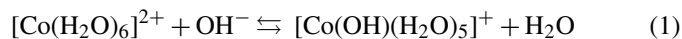


Fig. 2. Adsorption isotherms of Co(II) on humin at different pH values ($I = 0.05$ mol dm³ NaCl; 298 K).

tions increase. These isotherms are the result of a high affinity of HU for the adsorbate at low concentrations of Co(II) and a decrease in the number of available surface functional groups as the solute equilibrium concentration increases [20]. For L-type isotherms, the subgroup 1 indicates that the capacity of the theoretical monolayer does not reach saturation and, consequently the slope never reaches zero in the interval of concentration studied. The shape of subgroup 3 L-type isotherms is similar to that of subgroup 1 but with an exponential increase in the slope after the plateau. This increase is an indication of the appearance of a new mechanism in the retention, which is likely a surface precipitation process due to heterogeneous nucleation [21].

In accordance with the known chemistry of Co(II), as a function of pH, the following equilibrium equations for cobalt have been considered [36,37]:



To study the geometry and relative stability of these cobalt complex ions we have modeled them using the semi-empirical quantum method ZINDO/1. Fig. 3 shows the energetic profile for the hydroxylation reaction of the cobalt hexaaquocomplex as a function of pH. Both hydroxylation processes (Eqs. (1) and (2)) are exothermic. However, they are also both non-spontaneous and it is necessary to input energy into the system to activate them. Fig. 3 also presents the variation of the geometry as the reaction progresses. These substitutions of water for hydroxyl groups both follow a dissociative mechanism [38], implying the existence of the corresponding reaction intermediates. In the first hydroxylation reaction (Eq. (1)), $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, having O_h symmetry, gives rise to the monohydroxylated species with C_{4v} symmetry. The high reactivity of $[\text{Co}(\text{OH})(\text{H}_2\text{O})_5]^+$ [39] cannot be predicted by the energetic profile. However, the exchange of a water molecule for a hydroxyl group involves the approach of an OH group to the Co atom, and this causes the equatorial water molecules to move away from the metallic center. Simultaneously, the approach of the equatorial water molecules to the

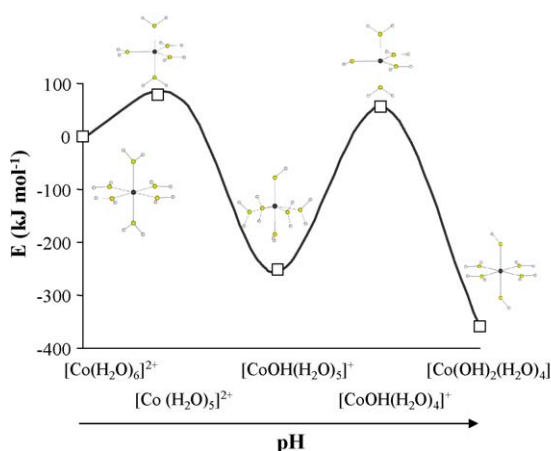


Fig. 3. Energetic profile for the hydroxylation reaction of cobalt hexaaquocomplex as a function of pH. Also shown is the variation of the geometry as the reaction progress.

apical one make it move away from the metallic center, decreasing its bond order, and facilitating its exchange for another OH group (Eq. (2)). This exchange gives rise to a product with D_{4h} symmetry, $[\text{Co}(\text{OH})_2(\text{H}_2\text{O})_4]$, that tends to dehydrate spontaneously to give the hydroxide (Eq. (3)).

To gain information about the most likely coordination of the different Co(II) species with HU surface groups, the different complexes that these cations can form with benzoic acid have been modeled, as it is a common surface component of HS. Fig. 4 shows the complexes obtained from the coordination of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ with one and two benzoic acid molecules, and the complex formed between $[\text{Co}(\text{OH})(\text{H}_2\text{O})_5]^+$ and one benzoic acid molecule. In all these cases, the ligand forms a six member chelate ring through the creation of an H-bond with one of the equatorial coordinated waters. The order of stability of these compounds is: $[\text{S-Co}(\text{OH})(\text{H}_2\text{O})_4] > [\text{S}_2\text{-Co}(\text{H}_2\text{O})_4] > [\text{S-Co}(\text{H}_2\text{O})_5]^+$.

Fig. 5 shows the electronic absorption spectra of supernatants of the sorption isotherm samples at different pH values, and with initial concentrations of $1280 \text{ mmol kg}^{-1}$. The spectra all show a broad band at $19,400 \text{ cm}^{-1}$, a well-defined shoulder at $21,500 \text{ cm}^{-1}$, and a small shoulder at $16,000 \text{ cm}^{-1}$ that is typical of the Co(II) hexaaquocomplex. The high-wavenumber shoulder can be assigned to spin-orbit coupling effects, ${}^4\text{T}_{1g} \rightarrow {}^2\text{A}_{1g}$ ($21,500 \text{ cm}^{-1}$) [40], while the other two bands can be assigned to ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})$ ($19,400 \text{ cm}^{-1}$) and ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}$ ($16,000 \text{ cm}^{-1}$) transitions. The lack of the observation of bands that can be assigned to the $[\text{Co}(\text{OH})(\text{H}_2\text{O})_5]^+$, even at pH 8, while bands of the hexaaquocomplex are observed, can be explained by the high reactivity of this species. Indeed, as soon as it is formed, it reacts with the surface functional groups of the adsorbent and is converted [6,19].

Thus, accounting for the chemistry of Co(II) complex ions in aqueous solution, and the relative stability of the different complexes they can form with simple organic ligands, it is possible to fit the sorption isotherm data presented here to a model that considers the global retention process as the sum of several single processes [4,6,19]. Chief among these processes are the

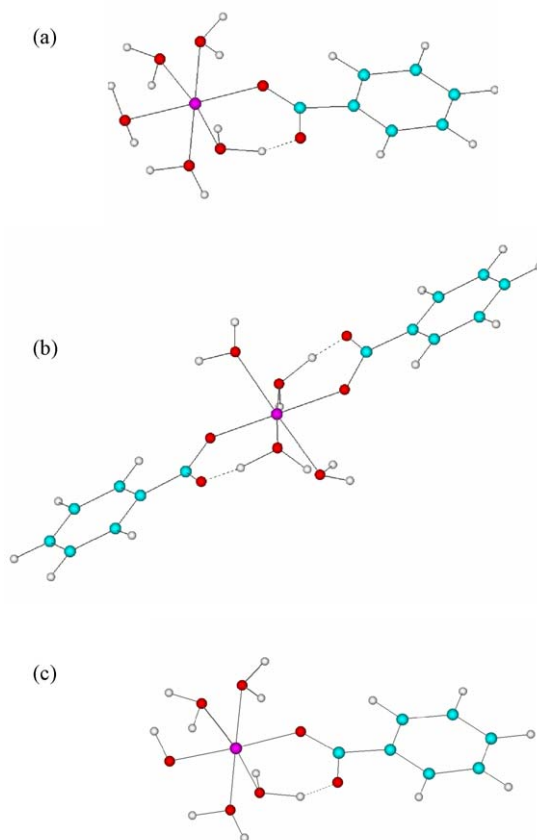


Fig. 4. Coordination complexes obtained from the coordination of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ with (a) one and (b) two benzoic acid molecules and (c) from the coordination of $[\text{Co}(\text{OH})(\text{H}_2\text{O})_5]^+$ with one benzoic acid.

following three:

Process 1—Adsorption of the cation $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$



Process 2—Adsorption of the cation $[\text{Co}(\text{OH})(\text{H}_2\text{O})_5]^+$

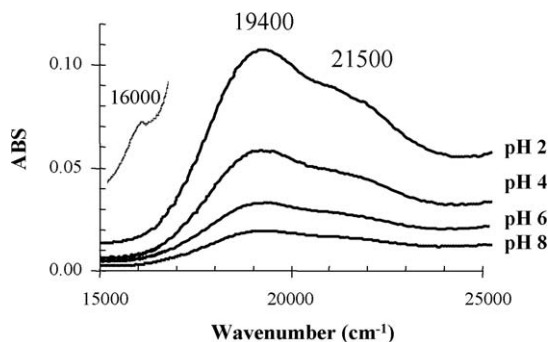
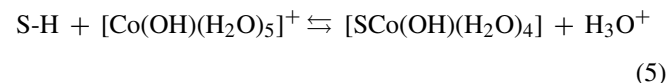
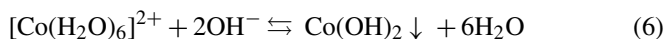


Fig. 5. Electronic absorption spectra of the supernatants of sorption isotherm samples, at different pH values, and with initial concentrations of $1280 \text{ mmol kg}^{-1}$.

Table 1
Parameters fit to Eq. (7)

pH	$n_{m(1)}^s$ (mmol kg ⁻¹)	K_1	$n_{m(1)}^s$ (mmol kg ⁻¹)	K_2	A	b	R^2
2.02 ± 0.03	39.0	0.59	0.50	0.467			0.9994
3.94 ± 0.02	45.6	2.74	133	1.30×10^{-2}			0.9993
5.94 ± 0.05	138	7.86	439	9.98×10^{-3}	4.08×10^{-8}	3.09	0.9999
7.95 ± 0.07	204	7.30	4.38×10^3	8.35×10^{-3}	7.38×10^{-6}	7.38	0.9998

Process 3—Precipitation of Co(OH)₂ on the solid surface



These lead to the following expression:

$$n^s = n_1^s + n_2^s + n_3^s = \frac{K_1 n_{m(1)}^s C_e}{1 + K_1 C_e} + \frac{K_2 n_{m(2)}^s C_e}{1 + K_2 C_e} + A C_e^b \quad (7)$$

where C_e is the equilibrium concentration of Co(II) species in water; K_1 , K_2 and A are the kinetic equilibrium constants for the two adsorption processes, and the surface precipitation, respectively; $n_{m(1)}^s$ and $n_{m(2)}^s$ are the maximum retention capacities for processes 1 and 2, respectively; b is the partial order for the precipitation process; n_1^s and n_2^s are the quantities (mmol) of Co(II) adsorbed per kg of HU as $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Co}(\text{OH})(\text{H}_2\text{O})_5]^+$, respectively; n_3^s is the quantity (mmol) of Co(II) precipitated on the solid surface as Co(OH)₂ per kg of HU.

The application of Eq. (7) to the sorption isotherms presented in Fig. 2 (continuous lines) leads to the results shown in Table 1. From these values, it is possible to calculate speciation diagrams that show the amount of metal retained on the surface of the HU, as a function of the initial amount of metal added, for various pH values (Fig. 6). These diagrams reveal the great selectivity that HU has for adsorbing different cobalt species [19]. This selectivity depends critically on pH and adsorptive concentrations. At pH 2 (Fig. 6a), the most important mechanism for the retention of Co(II) is the sorption of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$. $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ is

likely first retained electrostatically [41]. This then increases its effective concentration near the surface functional groups of the HU and facilitates its surface complexation with the carboxylic groups of the HU [6]. It is retained until saturation is reached. From pH 4 to 8 (Fig. 6b–d), the preferred retention mechanism is the surface complexation of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, and the amount of cobalt retained as $[\text{Co}(\text{OH})(\text{H}_2\text{O})_5]^+$ increases with initial concentrations of metal, due to the mass-action principle. At pH 8, however, surface precipitation also becomes an appreciable process of retention, and increases with initial concentrations of metals, likely because Co(II) specifically retained on HU surfaces acts as a seed for crystallization due to the great structural similarity of $[\text{S}-\text{Co}(\text{OH})(\text{H}_2\text{O})_4]$ and $[\text{Co}(\text{OH})_2(\text{H}_2\text{O})_4]$ [4,18].

Fig. 7 shows the FTIR spectra of the residues of selected points from the sorption isotherms, the hexaaquocomplex, and the hydroxide. $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_2$ is dominated by two strong bands, at 3405 and 1626 cm⁻¹, which can be assigned to the $\nu(\text{OH})$ and $\rho(\text{OH})$ of water coordinated to the metallic ion [42]. The cobalt hydroxide shows two bands in the $\nu(\text{O}-\text{H})$ region, as expected. The strong sharp band at 3632 cm⁻¹ can be assigned to a highly crystalline precipitate, while the strong broad band at 3545 cm⁻¹ is more likely from a turbostratic precipitate [43] and coordinated water (3462 cm⁻¹). This latter assignment is supported by data obtained using XRD (results not shown), and also by the presence of the $\rho(\text{OH})$ band at 1627 cm⁻¹. The bands at 1019 and 848 cm⁻¹ can be assigned to $\rho(\text{OH})$, while those at 668 and 500 cm⁻¹ can be assigned to $\nu(\text{MO})$. From pH

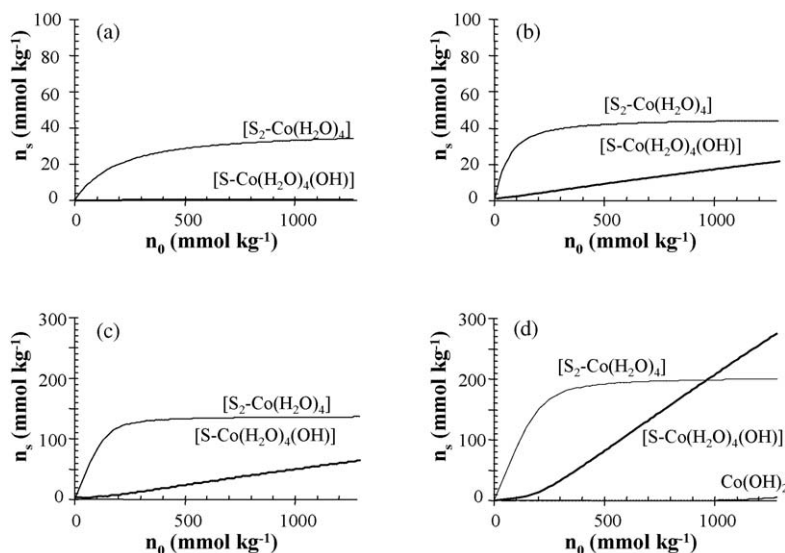


Fig. 6. Surface speciation of Co retention on HU at pH values of (a) 2.02, (b) 3.94, (c) 5.94 and (d) 7.95, as a function of initial metal concentration, and obtained applying Eq. (7).

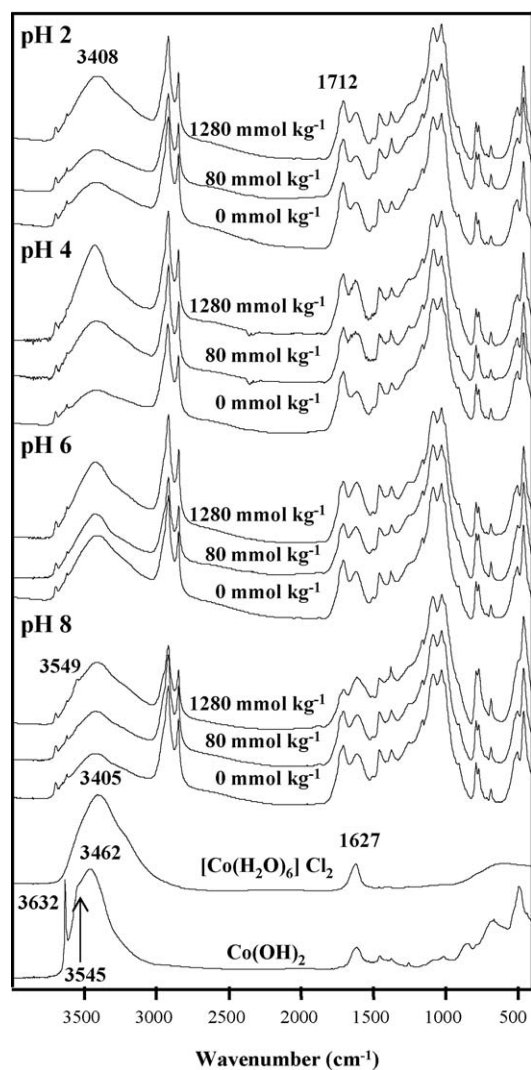


Fig. 7. FTIR spectra of the residues of selected points from the sorption isotherms of Co(II) on humin at constant pH ($I=0.05 \text{ mol dm}^{-3}$ NaCl, 298 K). Spectra of $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_2$ and $\text{Co}(\text{OH})_2$ are also included for comparison.

2 to 6, the FTIR spectra show increases in the band due to O–H stretching ($\sim 3400 \text{ cm}^{-1}$), and decreases in the band assigned to the C=O stretching of COOH ($\sim 1710 \text{ cm}^{-1}$), with increases in the initial amount of metal added. These variations are stronger

at pH 4, and suggest the formation of mixed Co complexes with water, hydroxyl groups and HU, in accordance with the mechanism suggested by the speciation diagrams presented (Fig. 4a and c).

At pH 8, the FTIR spectra show two unique phenomena. The increase in the O–H stretching band ($\sim 3400 \text{ cm}^{-1}$), and the significant decrease in the band assigned to the C=O stretching of COOH ($\sim 1710 \text{ cm}^{-1}$), with increased n_0 , suggests the surface complexation of both cobalt complex ions, $[\text{Co}(\text{H}_2\text{O})_6]$ and $[\text{Co}(\text{OH})(\text{H}_2\text{O})_5]^+$. On the other hand, the sample doped with $1280 \text{ mmol kg}^{-1}$ shows one weak peak at 3549 cm^{-1} sitting atop the O–H stretching band, suggesting the presence of an amorphous cobalt hydroxide, as supported by XRD data. The presence and location of the $\text{Co}(\text{OH})_2$ precipitate on the surface of HU was confirmed by means of Raman microspectroscopy. Fig. 8 shows an optical image of HU doped with $1280 \text{ mmol kg}^{-1}$ at pH 8, where Raman spectra were recorded at the indicated spots on the surface. Most of the surface gave no discernible Raman scattering signals, as they were obscured by the strong fluorescence of these highly aromatic samples (spots a and b are representative of this behavior). However, there are several small locations on the surface (spots c and d) that show bands at 679 , 474 and 190 cm^{-1} , due likely to $\nu(\text{MO})$ and $\rho(\text{MO})$ modes, that can be assigned to cobalt hydroxide. This demonstrates that the surface precipitation of Co on HU, predicted by our proposed model, occurs quite locally, rather than homogeneously on the entire solid surface.

4. Conclusions

In this work, the retention of cobalt on a humin (HU) derived from a brown coal has been studied using a wide variety of experimental techniques, including adsorption, speciation, UV–visible absorption, FTIR, XRD and Raman scattering. These, along with extensive computational modeling have been applied to further understand the complex interactions that HU and its surface components have with Co(II) species. It has been found that the selectivity that humin has for different Co(II) species, as well as the amount of Co(II) that it can retain, are both highly dependent on pH. Through Raman microspectroscopy measurements, the presence and location of $\text{Co}(\text{OH})_2$ precipi-

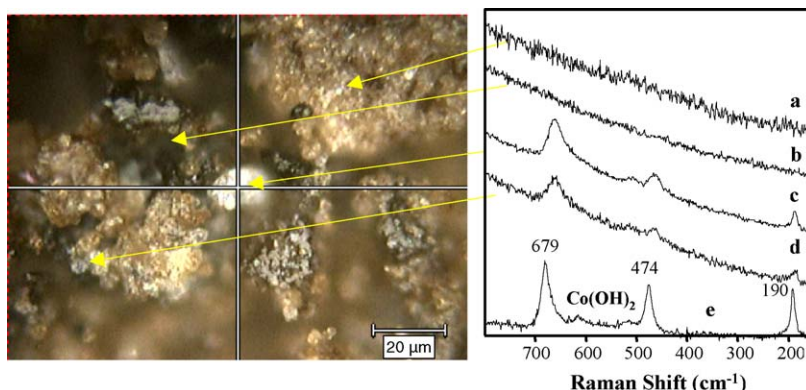


Fig. 8. Optical image of HU doped with $1280 \text{ mmol kg}^{-1}$ at pH 8, showing selected HU locations where Raman spectra were recorded from the surface (a–d). The Raman spectrum of $\text{Co}(\text{OH})_2$ is also shown (e).

tates on the surface of HU has been confirmed. It is expected that the results presented here will make a significant contribution to the fundamental understanding of the interactions that take place between humin and Co in the environment.

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