

## 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)<sub>2</sub> 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<sup>+</sup>, Sr<sup>2+</sup> and Gd<sup>3+</sup> 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 fractionated 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 N<sub>2</sub> (77 K) and CO<sub>2</sub> (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 ( $\zeta$ ) as a function of pH, a suspension containing  $0.1 \pm 0.0005$  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  $\zeta$  through Henry's equation [28].

### 2.2. Adsorption isotherms

Batch adsorption was carried out using scaled 50 cm<sup>3</sup> centrifuge tubes made out of low-density polyethylene. Samples of HU ( $0.2500 \pm 0.0005$  g) were suspended in 20 cm<sup>3</sup> 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  $298.0 \pm 0.2$  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 CoCl<sub>2</sub>·6H<sub>2</sub>O (Merck, analytical grade), with its ionic strength adjusted to 0.05 mol dm<sup>3</sup> using a 0.25 mol dm<sup>3</sup> NaCl solution. The volume was then set to 25 cm<sup>3</sup> 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  $\mu$ 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 CO<sub>2</sub> from the spectrophotometer, the transmission FTIR cell was flushed with N<sub>2</sub> gas for 10 min before scanning. The spectral resolution was set to 1 cm<sup>-1</sup> 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  $\sim 1 \mu$ m<sup>2</sup>. 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.

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