Interaction of Metals with Humic Acid Isolated from Oxidized Coal

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Abstract

The sorption behaviour of divalent cations M^{2+} (Cu, Pb and Zn) and trivalent cations M^{3+} (Fe, Al) with humic acid isolated from oxidized coal (Hazro,SE Anatolia,Turkey) was followed in aqueous solution.

Coal humic acid and metal ion interaction was investigated with special emphasis on the effects of pH, metal ion concentration and humic acid concentration. It has been found that the interaction of humic acid with metal ions in solution increases with pH, decreases with metal ion concentration and increases with humic acid concentration.

The differences in sorption ability of particular metal ions on oxidized coal-derived humic acid are Fe> Pb> Cu≥ Al> Zn and Fe> Pb> Al> Cu> Zn at pH 2.5 and 3.5, respectively, while they are Fe=Pb=Cu=Al> Zn at both pH 4.5 and 5.5.

The interaction of some trivalent (Fe, Al) and divalent(Cu, Pb, Zn) metal ions with humic acid prepared from coal was also studied using FTIR spectroscopy. This has proven helpful with respect to metal binding to understand better the potential sites of binding within the humic acid. Infrared spectroscopy showed the participation of COOH and OH groups in binding to the metal ions.

Keywords: soil pollution, humic, coal, sorption, cation

Introduction

The sorption characteristics of heavy metals in soil systems are important with respect to plant nutrition and environmental pollution, and this sorption process is influenced by the presence of organic matter. Cultivation of plants produced important variations in soil chemistry. The organic compounds released from plant roots can partially dissolve tightly bound forms of heavy metals, resulting in an increase of element uptake and decrease in concentration of some metals in contaminated urban soil [1-12]. Due to the presence of functional groups in their structures, humic substance (HS) is environmentally important in metal trapping and transport in the environment. Cation complexation by HS reduces bioavailability and toxicity. The increasing level of heavy metals in the environment represents a serious threat to human health, living resources and ecological systems.

The metal ion sorption capacity depends on the origin of humic substance and its pre-treatment. Humic acids (HAs) 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. HAs are present in low-rank coals and their chemical structure is modified as coalification progresses. With increasing maturity of coal, humic acid loses aliphatic side chains and oxygen-containing functional groups, particularly carboxyl and phenolic hydroxyl. These changes are accompanied by an increase in carbon content, molecular weight and aromacity [13-31].

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The HAs are always concerned with various intramolecular or cationic interactions [14]. To assess the molecular mechanisms, that is to say to characterize the structure of the interaction of the metal cations with the soil constituents especially with the organic matter, it is essential to use techniques of molecular spectroscopy [14, 15].

The mobility and transport of heavy metal ions in the environment is affected by the presence of HSs. The nature of the interaction between HA and cations in the environment is therefore of considerable importance. Although the exact structure of HA is not clear, the main functional groups present in a sample of HA are carboxylic acids, alcohols, phenols, carbonyls, phosphates, sulphates, amides, and sulfides. The complexation ability has been attributed particularly to carboxylic acid groups and phenolic OH goups, but amine groups may also be involved. Despite all of the active research over several decades, researchers are still far from agreement about the details of metal-HA interactions [16, 17].

HA is a chemically heterogeneous compound having different types of functional groups in different proportions and configurations. It contains carboxyl (-COOH), amine($-NH_2$), hydroxyl(-OH), and phenol(Ar-OH)functional groups, and has a negative charge in weakly acidic to basic media because of deprotonation [15]. The predominant functional groups in HAs are carboxyl, phenolic hydroxyls and alcoholic hydroxyls [31]. It is important to know the nature of organic functional groups of humic acid in the process of determining the stability of metal complexes. HA forms negatively charged complexes with heavy metal ions (especially Fe(III)). In accord with HSAB (hard and soft acids and bases) theory, Cu(II) and Pb(II) ions react with humic acid via O and N atoms and form stable complexes [24].

In the present study we have investigated the sorption of heavy metals by coal humic acid and determined how sorption is related to the solubility of the humic acid, pH and some concentration of background electrolyte.

Materials and Methods

HA is defined as the fraction of HS soluble in alkaline solution and insoluble in acidic solutions. The HA was obtained from coal from Hazro coal mine in Diyarbakir, SE Anatolia of Turkey. The coal sample was ground to pass through a 0.25 mm sieve. Prior to oxidation, the finely ground coal sample was partly demineralized. Demineralization was carried out by suspension of the coal in 0.5 mol L^{-1} HCl (1:10 w/v) for an hour at 25°C with mechanical stirring. The demineralized coal was oxidized at 200°C for four days in an air forced-circulation oven. The HA was extracted by suspending the oxidized coal samples in 0.5 mol L^{-1} NaOH (1:10 w/v) under nitrogen atmosphere at ambient temperature with mechanical stirring overnight. The suspension was centrifuged and then filtered and the filtrate was precipitated with 0.5 M HCl to a pH of 1. The precipitate was centrifuged, then filtered to speed the recovery of HAs. Any NaOH or HCl was removed by extensive washing with distilled water. The HAs obtained were dried in a vacuum oven at 105°C. Elemental analyses of carbon, hydrogen, nitrogen and sulfur were obtained with a Carlo Erba elemental analysis instrument model EA 1108. Oxygen was calculated by difference.

Stock solutions of Fe(III), Al(III),Cu(II), Pb(II) and Zn(II) were prepared from the respective nitrates of analytical grade purity in HNO_3 and water. The concentration of metals in the initial solution and the effluent were determined by an inductively coupled plasma atomic emission spectrometer(ICP-AES). The pH of the solutions for Fe(III), Al(III), Cu(II), Pb(II) and Zn(II) was adjusted with nitric acid and ammonia. The experimental concentrations of metal ions studied are 5×10^{-4}, 1×10^{-4}, and 5×10^{-5} M in the pH range from 2.5 to 5.5. The HAs were weighed, ranging from 50-1000 mg, into clean, acid-washed 100 cm^3 glass vials. Deionized water and varying amounts of stock metal nitrate solutions were added to the vials. Following dilution to a final total volume of 100 cm^3, the solutions were stirred at 25°C for 2 hours. The contents of the vials were centrifuged for 30 minutes at 4000 rpm and then filtered. The metal content of the filtrates were then determined by ICP-AES. For metal ion measurements a Leeman Labs Inc PS 950 model ICP-AES was used. The pH measurements were made with a Mettler Toledo MPC 227 model digital pH-meter. All experiments were done in triplicate.

The metal-humate complexes (HA-M) were obtained by ion exchange of solid HA with 0.025 M solutions of metal ions at pH 5.1 from acetate buffer. The solutions were prepared from nitrate salts of the studied cations. For FTIR experiments.1g mass of finely powdered HA placed in 200 cc beaker 100cc of 0.025M metal salt solution was added. The suspension was magnetically stirred at 60°C for half an hour and then left for 24 h to saturate with the metal ion. Resulting suspensions of HA-M complexes were filtered and rinsed with distilled water. Finally the solid complexes were dried at 80°C for 4 h. The dry complexes were analyzed by FTIR.

All chemicals used in this work were of analytical grade. All aqueous solutions were prepared with distilled deionized water, which was purified by a Millipore Milli-Q water purification system.
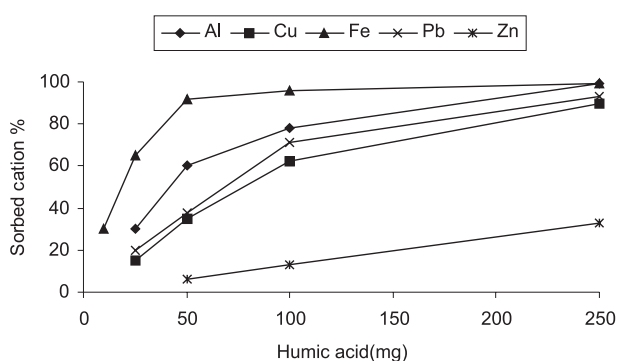
Infrared spectra were recorded in a MIDAC 1700 model FTIR spectrometer in KBr pellets. Good quality spectra were obtained by 100 scans at 2 cm^{-1} resolution. KBr pellets were pressed under 20MPa pressure. Pellets were dried at 105°C for 2 d.

Results and Discussion

The HA used in this study was isolated from Hazro coal [19] in Diyarbakir, Turkey, and characterized in our laboratory as previously reported [18]. The elemental
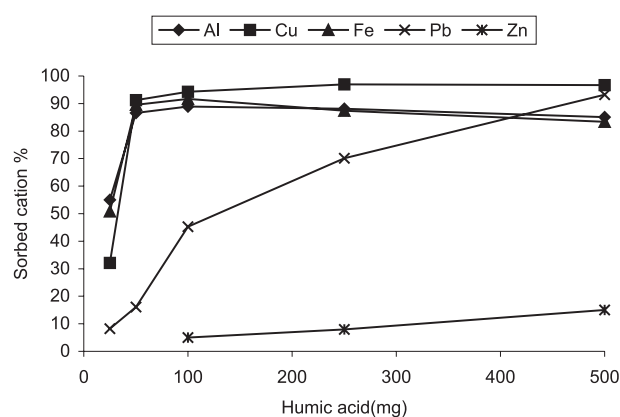
Table 1. Main characteristics of humic acid.

Elemental analysis		Atomic ratios		Acidity (meq g⁻¹)		Yield(%)
Ash	5.3	H/C	0.039	-COOH	3.0	65.7
Carbon	60.8	N/C	0.026	ø-OH	2.9	
Hydrogen	2.4	O/C	0.58	Total	5.9	
Nitrogen	1.6					
Sulfur	0					
Oxygen(diff)	35.2					

Fig. 1. Effect of the quantity of humic acid on the sorption of metal cations onto humic acid at pH 2.5 ($[M^{n+}]=5.10^{-4}$ M).

Fig. 2. Effect of the quantity of humic acid on the sorption of metal cations onto humic acid at pH 5.5 ($[M^{n+}]=5.10^{-4}$ M).

composition and atomic ratios of the oxidized coal derived humic acid are listed in Table 1. Molar ratios such as H/C, N/C and O/C can provide vital structural information. The general low values for H/C suggest condensed aromatic ring structures, while the high O/C ratios may be indicative of the degree of oxygen substitution in this structure [10].

The sorption behavior of divalent (Cu, Pb, Zn) and trivalent cations (Fe, Al) with HA-extracted fraction of coal was followed in aqueous solution. HA acts as a ligand of great capacity to form complexes with metals in natural environments. HA plays the role of a multidentate proligand with several reactive donor sites for coordination to a variety of metal ions [21]. The metal ion sorption capacity depends on the origin of HS and its pretreatment. We studied the sorption of heavy metals by HA and determined how sorption is related to the solubility of the HA, pH and the concentration of background electrolyte. This information will allow a better understanding of the likely fate of heavy metals in the soil environment and hence their availability to plants and their transport to groundwaters. The major mechanisms by which HA adsorbs onto mineral surfaces have been proposed to involve:

(i) anion exchange (electrostatic interaction),
(ii) ligand exchange surface complexing,
(iii) hydrophobic interaction,
(iv) entropic effects,
(v) hydrogen bonding, and
(vi) cation bridging [31].

We have found that the interaction of HA with metal cations increases with pH, decreases with metal ion concentration, and increases with HA concentration (Figs. 1, 2). The differences in sorption ability of particular metal ions on oxidized coal-derived humic acid may be illustrated by the series: Fe> Pb> Cu≥ Al> Zn, Fe> Pb> Al> Cu> Zn at pH2.5 and 3.5, respectively, while they are Fe =Pb=Cu=Al> Zn at pH4.5 and 5.5 (Table 2).

FTIR spectra of humic acid and metal- humate complexes provide information on structure, functional groups and information of modes of complexes. The most interesting bands in which oxygen-containing functional groups carboxylic acid and phenolic are responsible for metal ion binding are discussed in detail. FTIR spectra were collected for humic acid –metal complexes of Cu, Pb, Zn, Al, Fe and absorption frequency assignments are given in Table 3.

The qualitative data for coal-derived HA permit to identify:
– Intense localized band at 3416 cm⁻¹ assigned to O-H and N-H stretching from different sources.
– Double band at 2920 cm⁻¹, this band attributed to aliphatic C-H bands for which deformation appears at 1450 cm⁻¹.
– In the 1680-1750 cm⁻¹ region, a sharp band appears at 1702 cm⁻¹.This could be attributed to C=O stretching vibrations due to carboxylic groups.

Table 2. Effect of pH on the sorption of metal cations onto humic acid.

Metal*	pH 2.5			pH 3.5		pH 4.5		pH 5.5	pH 5.5
	HA (mg)								
	1000	250	100	500	100	250	50	250	0
	Sorption%								
Fe	85	74	57	97	92	97	96	100	79**
Pb	64	42	11	93	28	93	38	99	20**
Cu	61	32	9	83	20	90	35	97	50**
Al	60	26	10	95	52	99	60	100	35**
Zn	14	9	8	37	13	33	6	60	0**

*Cation concentration 5×10^{-4} M
** Insoluble hydroxide compounds.

Table 3. Major infrared absorption bands (cm^{-1}) for Hazro humic acid (HA) and its metal complexes.

Hazro HA	3416(br)*, 2925(w), 1702(m), 1620(m), 1394(w), 1220(m), 1032(w), 768(w)
Cu-humate	3400(br), 2950(w), 1590(st), 1370(w), 1230(w), 1020(w), 750(w), 660(w)
Pb-humate	3415 (br), 2925(w), 1585(st), 1558(m), 1385(w), 680(w)
Zn-humate	3405(br), 2920(w), 1696(w), 1595(m), 1364(w), 1225(w), 1040(w), 665(w)
Fe-humate	3415(br), 2910(w), 1595(st), 1375(w), 1240(w), 1035(w), 665(w)
Al-humate	3405(br), 2920(w), 1610(st), 1230(w), 665(w)

* br = broad, m = medium, st = strong, w = weak

– 1600-1650 cm^{-1} region is attributed to C=C band, C=O and COO- groups.
– The band appearing at 1230 cm^{-1} in the 1100-1300 cm^{-1} region could be assigned to C-O stretching vibrations and OH deformation due to carboxylic groups [18].

The 3416 cm^{-1} band, ascribed to vibration of the phenolic groups of the HA-Me preparations, occurs within the range of 3410-3400 cm^{-1}. Its intensity is higher than in respective spectra of humic acids. These bands in the spectra of all metal-humate preparations result from the occurrence of hydration water. The examined metal ions and humic acid produce aqua-complexes. HA-Al gave rise to the most intense absorption bands. A very different six-membered ring likely will form, in which the Al(III) will be coordinated to the phenolic oxygen and the deprotonated oxygen atom of the carboxylic acid. The carbonyl oxygen atom of the carboxylic acid is not involved in the coordination of Al(III). The IR spectra of metal-humic samples proved that all the examined metal ions form metal-humic hyrocomplex compounds. The largest amounts of hydrating water is included in humic hydrocomplex of Al. HA-Pb and HA-Cu give rise to the weakest absorption in the 3410-3400 cm^{-1} region.

Generally, the most important characteristic of the IR spectra of humic substances is an absorbtion peak at about 1700 cm^{-1} assigned to C=O stretching. Reaction between metal ion and COOH functional groups, forming a metal ion complex, results in the disappearance of the 1702 cm^{-1} absorption band and the appearance of new bands at about 1600cm^{-1} (symmetric COO- stretching) and 1380 cm^{-1}(antisymmetric COO- stretching). The disappearance of this band also suggests that most of the COOH groups were converted to the COO⁻ form. Complexes showed a band in the 1230-1240 cm^{-1} region except for Pb ion with respect to the band at 1220 cm^{-1} for the free acid. This band is assigned to C=O stretching and OH deformation of COOH, which suggests that not all COOH groups were converted to COO⁻ or reacted with metal ion[29]. IR spectra of the Zn complex showed only slight counters of the 1702 and 1220 cm^{-1} bands, suggesting that not all COOH groups take part in ion exchange.

The FTIR spectral analyses indicate that cations Al(III) and Fe(III) appear to be bound to humic acid primarily through carboxyl- functional groups, while Pb(II) apparently are bound through carboxyl and alcoholic moieties. Cu(II) is bound preferentially to oxygen- and nitrogen-containing functional groups.

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