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FTIR - A Didactic Approach for the Study of Humic Acid - Chromium Chelation During the Environmental Remediation

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Abstract. The present study uses infra-red spectroscopy as a didactic approach to characterize the chromium-humic acid interaction. Shifts of the characteristic carboxylate peaks in the IR spectrum of humic acid upon its interaction with chromium are noted. These changes have been interpreted to conclude that binding of chromium to humic acid is through these groups. An analytical grade humic acid was used for this study. It was also concluded that at the moderate pH i.e 8.5 all the waste chromium ions were cleared from waste water controlling the water pH.

Keywords: IR study, humic acid, chelation, chromium binding

Introduction

Humic acids (HA) isolated from coals using an alkaline solution, are very complexed organic macromolecules with acid functional groups, primarily carboxylic acids and phenols as well as carbonyls, amines, aromatic and aliphatic carbons. Humic acid binds heavy metals due to its higher content of oxygen-containing functional groups (Casas and Martin, 1997), which can form stable complexes with metals as Cu(II), Hg(II), Cd(II), Cr(III) etc. This binding capacity has been demonstrated in several studies (Yasser *et al.,* 2011; Dragan and Fitch, 1998). It is found that humic substances can reduce the concentration of free metals ions in waters (Stackhouse and Benson, 1989).

In a reported experiment (Holman *et al.,* 2002), the lead complex band shift for C=O from 1670 cm^{-1} for the free ligand to 1537 cm^{-1} and another similar experiment (Tharanitharan and Srinivasan, 2009) was designed in which the FTIR spectrum of free EDTA was compared with that of lead EDTA identifying the changes in C=O produced by EDTA-lead complexation. Many more experiments involving the synthesis and study of the FTIR spectra of carbonylcontaining organometallic compounds are now proposed as laboratory experiments. The binding sites for Cu, Cd, and Pb are strongly related to the humic substance content of extracellular polymers (ECP) in activated sludge (Guibaud *et al.,* 2003). The stability of ECP-metal complexes followed the order Cd > Pb ~ Cu and the metallic ions are bonded to acidic groups of humic acid (Boyd *et al.,* 1981). In that way, carboxylate has been identified as the group mainly responsible for chelation between humic substances and metallic ions (Holman *et al.,* 2002). This is because lone-electron pairs on the oxygen atom can produce a coordinate bond with the empty d-orbitals in heavy metals. This chelation produces changes in position and intensity of the characteristic IR absorption bands in the ranges around 1700 cm^{-1} and 1600 cm^{-1}.

Complexes between 2,5-dihydroxybenzoate and heavy metals including Cd(II) using IR and electronic spectroscopy showed octahedral coordination with the heavy metal bound to two monodenate carboxylate groups in the trans position and 4 water molecules (Micera and Erre, 1992). On the basis of the latter, one hypothesis that can be established is that carboxyl and carboxylate groups in the humic material are responsible for Cd complexation, which is evidenced by displacements of the symmetric and asymmetric stretching vibration of the COOH and COO$^-$groups.

A better understanding of interaction between metal-organic ligand is one of the key issues in soil science today.

Advanced analytical techniques, such as atomic absorption spectrometry alone cannot play proper role in the study of heavy metal interactions with coal constituents. Therefore, infrared studies may support in the understanding and reviewing of interior of

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molecular lattice by the help of characteristics IR absorption spectral bands giving clear picture of how the metal ions are retained by humic acid.

In an earlier study its potential use for chromium removal from waste waters has been discribed. For present study humic acid isolated from Lakhra lignite coal was used. Chelation between Cr^{3+} and HA was studied using FTIR spectroscopy to identify the functional groups involved in complex formation, possible multidentate character of the ligands, and the effects of pH as well as addition of increasing amounts of Cr(III) on the IR bands associated with carbonyl symmetric and asymmetric stretching.

Materials and Methods

Material. Analytical grade humic acid standard from Sigma Aldrich Company was used.

Preparation for FTIR spectra. At the first step, the effect of pH on the humic acid FTIR spectra was determined.Two samples of dried HA (100 mg) were placed in test tubes. The first tube was filled with 20 mL of distilled water. To the second tube 10 mL of distilled water was added and the pH was adjusted to 7.5 with 0.1 M NaOH. Additional water was added to a final volume of 20 mL. Both tubes were agitated for 1h: centrifuged and the supernatant was discharged. The solid residue was washed three times with distilled water and dried in an electric oven at 40 °C for 12 h. FTIR spectra were then recorded.

Humic acid chromium chelation. The effect of Cr^{3+} chelation with humic acid was determined through FTIR spectra. Into five test tubes, 100 mg of HA was placed along with 10 mL of 0.0002 M, 0.002 M, 0.02 M, 0.2 M and 0.5 M Chromium sulphate $Cr_2(SO4)_3$ solution, respectively. Suspensions were agitated for 12 h, and supernatant was removed after centrifugation. These supernatants were then tested for reduction of Cr^{3+} ions at atomic absorption spectrometer (Table 1). Solid residues were washed three times with distilled water and dried in an electric oven at 40 °C for 12 h. All infrared spectra of HA and Cr-HA recorded using KBr discs (ca. 1%) at Thermo-Nicolet Model 6700 FTIR in the region of 3500 to 400 cm^{-1} at a 2 cm^{-1} resolution.

Results and Discussion

The possible models explaining how binding takes place involve functional groups (Table 2-3), coordinate bonds, electronic attractions between positive and negative species, chelation and surface electric charge of colloidal materials.

Oxygen containing functional groups i.e. carboxylic acids and carboxylates are mainly responsible for this chelation in large number of mono and multidentate ligands. These compounds can be synthesized and, by observing the positions, shapes and displacements of their characteristic absorption bands around 1800 and 1600 cm^{-1}, can predict possible coordination mode.

Table 4-5 show actual picture of the active functional groups involved and describe their participation through different respective bands for expected chelation. The results identified the most important features of the FTIR spectra of humic acids at pH 5.5 (Fig1a), which are (a) an intense and broad band between 3500 and 3100 cm^{-1}due to the stretch of various hydroxyl and N-H

Table 1. Complexation(Ahmed *et al.,* 2006) in µg/mL of Cr^{3+} by humic acid (pH- 3.53 to 8.5)

$[Cr^{3+}]$ initial	$[Cr^{3+}]$ final	$\Delta [Cr^{3+}]$	Cr^{3+} adsorbed (%)	mg C_r^{3+} adsorbed per g HA
100	79	21	21	210
200	162	38	19	190
300	239.1	60.9	20.3	203
600	467	140	23.3	233

Table 2. Elemental composition of humic acid

Element	Humic acid (wt %)
C	53.6 – 58.7
H	3.2 – 6.2
N	0.8 – 5.5
O	32.8 – 38.3
S	0.1 – 1.5

Table 3. Estimated functional groups in humic acid (m. mol/g).

Functional group	Humic acid
Total acidic groups	5.6 – 8.9
Carboxyl COOH	1.5 – 5.7
Phenolic OH	2.1 – 5.7
Alcoholic OH	0.2 – 4.9
Quinoid / keto C = O	0.1 – 5.6
Methoxy OCH_3	0.3 – 0.8

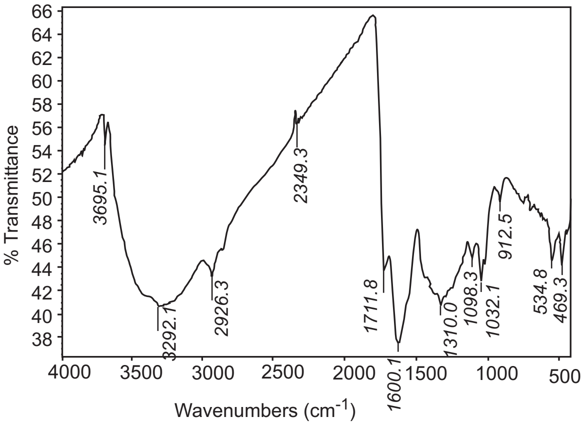

Fig. 1a. Humic acid at pH 5.5.

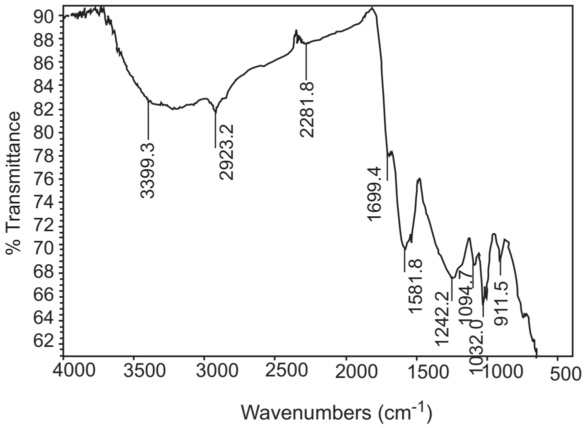

Fig. 1b. Humic acid Spectra pH 7.5.

functional groups; (b) peaks of variable intensity between 2930 and 2855 cm^{-1} and between 2855 and 2850 cm^{-1}, which are associated with aliphatic C-H symmetric and asymmetric stretching; (c) absorption bands at 1711.8 (COOH), 1600.1(υ_s(COO$^-$)) and 1310 cm^{-1} (υ_a(COO) and OH in COOH group) which indicated the presence of both symmetric and asymmetric stretching vibrations of –COOH and –COO$^-$ and (d) an asymmetric stretching vibration around 1032 and 912.5 cm^{-1}, which indicated the presence of skeletal C–C vibrations. Spectra have also been reported (Micera and Erre, 1992; Boyd *et al.,* 1981) for humic substances, found absorption bands for carboxylic acids and carboxylates.

The FTIR spectrum suggested the existence of both dissociated and undissociated forms of carboxylic acids when humic acid are at pH 5.5 (Fig. 1a).

Figure 1b indicates changes observed in FTIR spectra providing evidence for the shifting of the equilibrium, on increasing pH 5.5 to pH 7.5. The intensity of the 1711.8 cm^{-1} band is reduced as ionized carboxyl groups increased. A displacement is also observed in the asymmetric vibration band of the carboxylate anion from 1600.1 to 1581.8 cm^{-1} with a parallel shift to frequencies (1310 to 1242.2 cm^{-1} and 1098.3 to 1094.7 cm^{-1}) for C–O stretch. All the experiments were conducted quantitatively with the same amount of humic acid in each case to compare the intensities of the bands.

Figure 2-7 reflect the effect of Cr^{3+} addition on the FTIR spectra of humic acids suspension, indicating similar changes to those produced by pH. The absorption band at 1700 cm^{-1} is progressively displaced to lower frequencies until it disappeared at the highest Cr^{3+} concentration.

Table 4. IR spectral assignments for the humic acid and Cr-humic acid Complex

Compounds	Peaks of Humic acid and Cr^{3+} complexes (cm^{-1})	Tentative assignments
	3500 – 3100	Due to presence of various OH groups
Humic acid (HA) at pH 5.5)	2926.3 – 2855 and 2855 – 2850 1711.8, 1600.1 and 1310 1032 and 912.5	Aliphatic C-H stretch -COOH, –COO$^-$ and C=O C-C skeleton, Si-O silicate impurities
Humic acid HA at pH 7.5	1600.1 – 1581.8 1310 – 1242.2 1098.3 – 1094.7	-COOH and C=O vibration -COOH and C=O vibration C-O
Chromium – HA complex	Band at 1700 disappeared at higher concentrations of Cr^{3+} Shifting of 1586.4 – 1581.2	Due to complexation Ionization of carboxylic acid occurred
Cr^{3+} concentration 0.0002M – 0.5M	1245.7 moved to 1251.4 and 1272.1	Complexing of higher concentration of Cr^{3+} Deformation vibration of OH in COOH group and υ_s(COO$^-$)

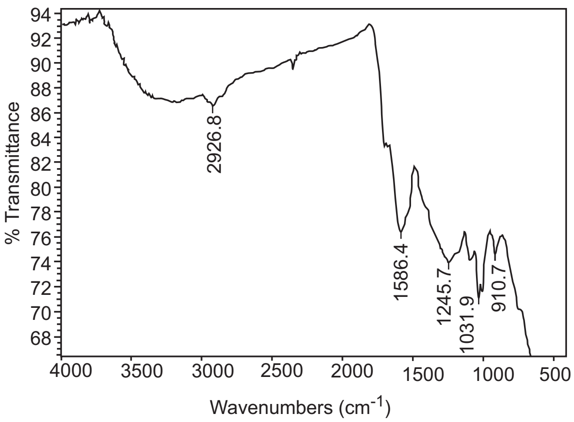

Fig. 2. Spectra IR for sample A-1 (Complexed with 0.0002M Cr^{3+})

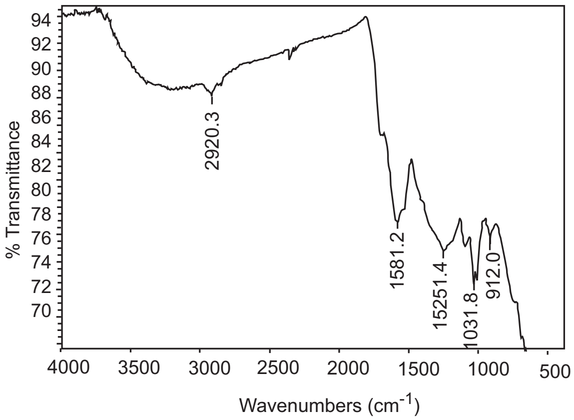

Fig. 3. Spectra IR for sample B-1 (Complexed with 0.002M Cr^{3+}).

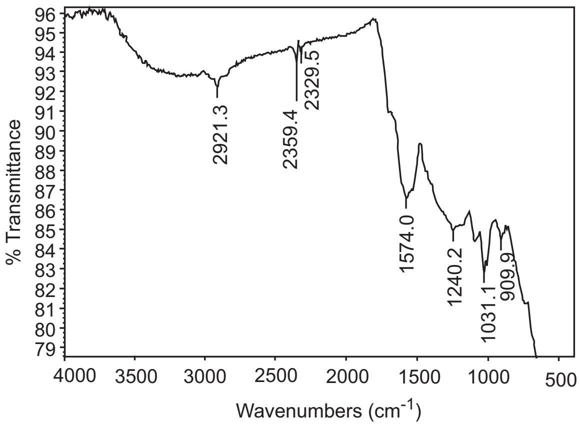

Fig. 4. Spectra of IR for Sample C-1 (Complexed with 0.02M Cr^{3+}).

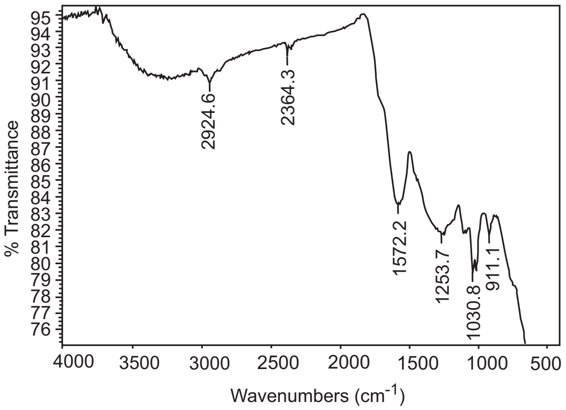

Fig. 5. Spectra of IR for Sample D-1 (Complexed with 0.2 M Cr^{3+})

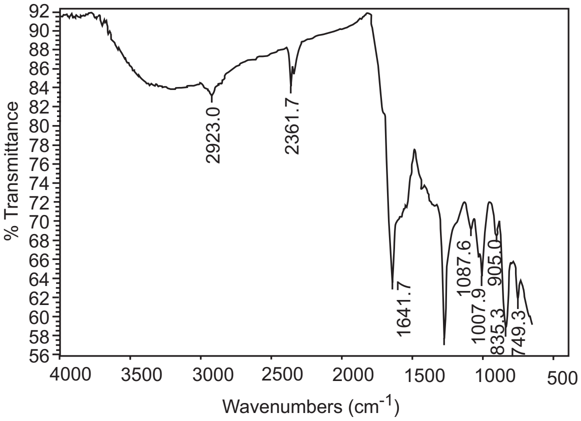

Fig. 6. Spectra IR for sample E-1 (Complexed with 0.5 M Cr^{3+}).

Also, shifts from 1586.4 to 1581.2 cm^{-1} in υ_S (COO^-), consistent with ionization of carboxylic acids, occurred. It is observed that both neutralization and metal complexation induced the conversion of –COOH to COO, is evidenced by the disappearance of the 1711.8 cm^{-1} band. The absorption band for the symmetric stretching vibration also changed but to a higher frequency. These results showed that,addition of Cr^{3+} in increased amounts, effectively, induced the ionization to the carboxylic acids followed by chromium coordination to the centre of negative charge (Table 1).

It is necessary to differentiate between the possible types of complexes between carboxylate and Cr^{3+}. Separation between the asymmetric υ_a(COO^-) and symmetric υ_S(COO^-) stretching frequencies is related to the mode of complexation.

In monodentate complexes (I) the separation between υ_a(COO^-) and υ_S(COO^-) is larger than in uncomplexed carboxylate ion. On the other hand, in chelate complexes, the separation is smaller than in free carboxylate, and in structure III or bridging complexes, the separation is similar to that of uncomplexed carboxylate. If it is

Table 5. Carboxylate stretching frequencies of HA at pH 7.5 and Cr- HA

	υs(COO^{-}) (cm^{-1})	υa(COO^{-}) (cm^{-1})	Δ (cm^{-1})	Structure
HA (pH = 7.5)	1581.8	1242.2	339.6	Uncomplexed
Cr-HA	1641.7	1272.1	396.6	Bidentate

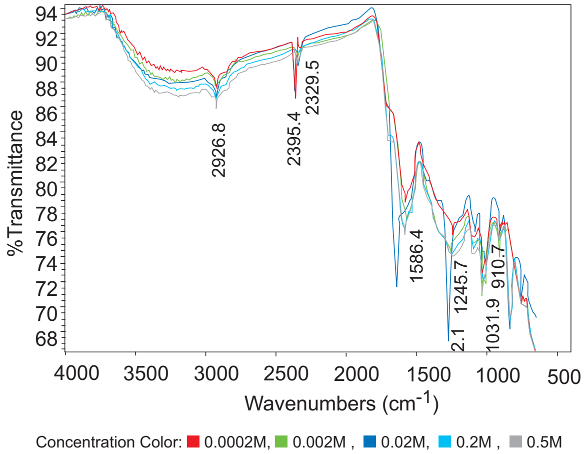

Fig. 7. Summarized spectra IR for humic acid chromium complex.

considered that at pH 7.5 most of the carboxylic acid had been ionized, the absorption bands υa(COO^{-}) and υs(COO^{-}) for HA are identified as uncomplexed (Table 2) where Cr-HA is referred to as a chromium-humic acid complex. The separation value is lower in Cr-HA than in the uncomplexed form; showing a bidentate character to the complexation between organic ligand and metallic ion (Boyd *et al.,* 1981).

In this study, it was observed that HA adsorbed chromium ions. Ionic concentrations were reduced effectively, (Table 3) proportional to the initial concentration.

Conclusion

The present study uses infra-red spectroscopy as a didactic approach to characterize the chromium-humic acid interaction. Shifts of the characteristic carboxylate peaks in the IR spectrum of humic acid upon its interaction with chromium are noted. These changes have been interpreted to conclude that binding of chromium to humic acid is through these groups.

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