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The Interaction of Soil Fulvic Acid and Chromium(VI) Produces Relatively Long-lived, Water Soluble Chromium(V) Species

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Abstract

Soil-derived fulvic acid reacts with chromium(VI) in water in the pH range 3 to 12 to produce chromium(V) species detected by their EPR spectra for periods of 1 to 2 days.

Introduction

The humic substances present in soils form the most abundant form of organic matter at the Earth's surface and play an essential role in soil fertility. Much effort has been directed towards the study of these complex materials but their nature is still incompletely understood [1, 2]. The soluble humic materials obtained by alkali extraction of soils are conventionally divided into two main groups: humic acids (HA) which are precipitated by acidification of the alkali extracts, and fulvic acids (FA) which form the acid-soluble fraction.

Information about the interactions of metal ions with humic substances is important both for an understanding of the soil retention, transport and bio-availability of those metal ions required in life processes and also for those which are harmful and, therefore, constitute an ecological hazard.

Compounds of chromium(VI) which have extensive industrial use, present a potential environmental danger because of their mammalian carcinogenicity and toxicity [3–6]. We recently found [7] that chromium(VI) is reduced by humic acid in aqueous solution to chromium(V) and that such species persist for several days before decaying completely to the final chromium(III) state. Such chromium(V) species are of interest in view of the suggestion [8] that chromium(V) may be involved in chromium carcinogenicity.

Although the precise nature of the fulvic acid fraction of soil humic material is still a matter of active debate [9] it is generally accepted that the components of FA probably have lower average molecular weights than the HA fraction. This fact and the aqueous solubility of FA over a wider pH range than that of HA prompted us to examine by EPR spectroscopy the interaction of the FA fraction with Cr(VI) for comparison with the HA/Cr(VI) combination. We report here the results of that study.

Experimental

The source of chromium(VI) was potassium dichromate of AnalaR grade. Samples of fulvic acid were obtained from two different soils using different extraction methods.

FA1

Yorkshire peat (25 g)* was saturated overnight in HCl (1 M) and then washed with water (the washings were retained). The soil was then extracted with NaOH (0.5 M, 150 cm^3) and the pH then adjusted to 1 using HCl. The supernatant liquid after filtration was combined with the washings from the first stage and the combined solution passed down an Amberlite XAD-8 column, the resin being in its protonated form [2]. The FA retained on the column was eluted with NaOH (0.01 M) to give a wine-red eluant. Evaporation gave a dark-brown solid.

FA2

Thames Valley soil (50 g) was extracted overnight with an alkaline solution (500 cm^3) of NaOH (0.1 M) and sodium pyrophosphate (0.1 M). The filtered extract was acidified to pH 1 with sulphuric acid, heated for 30 min at 80 °C to coagulate the HA, and then filtered. The straw-yellow filtrate was passed through activated charcoal [10]. The charcoal containing the FA was washed several times on the funnel with water, until the washings were less acidic (pH ~ 3.8). The FA was removed from the charcoal by the addition of small amounts of cold NaOH (0.2 M). The filtrate was wine-red, and gave a buff-coloured solid on evaporation.

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The EPR studies were made at X-band frequency (*ca.* 9.5 GHz) using the apparatus described previously [7] and with solutions containing potassium dichromate (0.125 M) and FA (0.7 g l^{-1}) adjusted to the desired pH with sodium hydroxide.

Results and Discussion

The EPR spectra of the solid FA samples isolated from the two different soils (see 'Experimental') each showed the expected [11] free radical signal at $g \approx 2.005$.

The EPR spectra in the $g = 2$ region of aqueous solutions of FA1 and potassium dichromate at various pH values in the range 4–12 are shown in Fig. 1 (All spectra in Fig. 1 are with constant concentrations of FA1 (0.7 g l^{-1}) and $K_2Cr_2O_7$ (0.125 M) and constant spectrometer settings to aid direct comparison). At pH 4 (Fig. 1a) a sharp (0.05 mT linewidth) signal due to chromium(V) was observed at $g = 1.981$ accompanied by four hyperfine bands due to ^{53}Cr (9.55% abundance, $I = 3/2$) at 1.9 mT spacing.

The simplicity of this Cr(V) band contrasts with the more complex spectra found for Cr(V) generated from Cr(VI)/HA reactions for which at least three components were observed with g values of 1.984, 1.979 and 1.972 [7]. This difference did not arise from a particular feature of the soil from which the FA was derived or its method of separation as FA2 (from a different soil source and extraction method) gave the same results. The simplicity of the Cr(V)/FA spectra presumably reflects a simpler set of reducing ligand systems in the FA fraction of humic material than in the HA component. This would be in accord with the generally accepted view of higher complexity for HA.

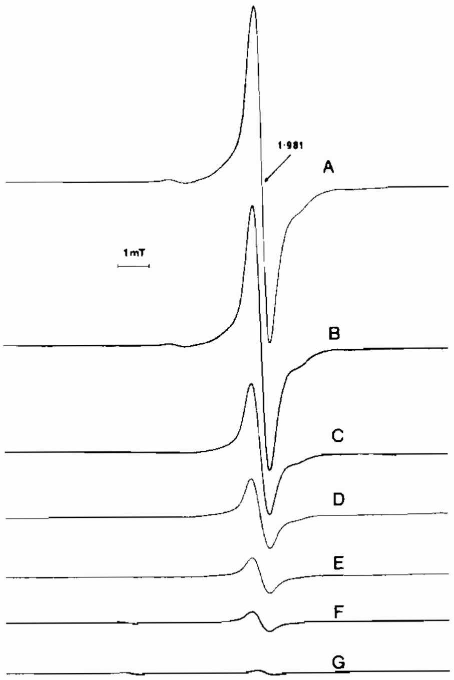

Fig. 1. X-band EPR spectra in the $g \approx 2$ region of aqueous solutions of fulvic acid (0.7 g l^{-1}) and $K_2Cr_2O_7$ (0.125 M) at: (a) pH = 4; (b) pH = 5; (c) pH = 6; (d) pH = 7; (e) pH = 8; (f) pH = 9.4; (g) pH = 12.1.

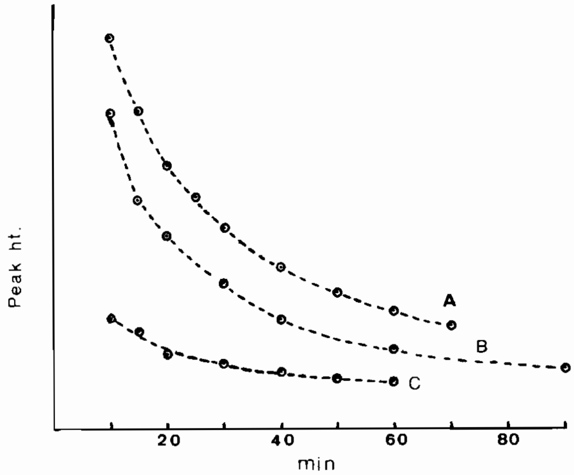

Fig. 2. Time dependence of the intensity (relative peak-to-peak heights of the $g = 1.981$ band) of the Cr(V)/FA species at: (a) pH = 3.15–3.48; (b) pH = 4.25; (c) pH = 5.2.

The ^{53}Cr hyperfine coupling constant for Cr(V)/FA of 1.9 mT (1.78×10^{-3} cm^{-1}) is very close to the values found [12] for other Cr(V) complexes with oxygen-donor ligands such as 5′-AMP ($A = 1.69 \times 10^{-3}$ cm^{-1}) or 2-ethyl-2-hydroxybutyrate [13] ($A = 1.75 \times 10^{-3}$ cm^{-1}). This oxygen-donor environment about the Cr(V) is to be expected from the hydroxyl-substituted polycarboxylic acid nature of FA [9].

The Cr(V) signal diminished in intensity as the pH was raised (Figs. 1b–g) but it could still be detected at a pH of 12 (Fig. 1g) and was unchanged in position throughout the pH variation. The FA free radical signal at $g = 2.005$ was not observed in the solution spectra at pH < 9 because of the relatively low concentrations of FA we employed, but it was observed weakly at the highest pH values. A marked increase in the free radical signal of FA on increasing the pH from 7 to 11 or more was observed by Senesi and Schnitzer [13].

The intensity of the Cr(V) signal decreased with time, the rate of decrease being greater at low pH values (Fig. 2). The time decay of the Cr(V)/FA species was faster than had previously been observed for the Cr(V)/HA system [7], but, even so, Cr(V)/FA signals could still be detected in solutions stored at pH 4 for up to 24 h.

At initial pH values in the range 3–4, the decay of the Cr(V) signal was accompanied by a slight

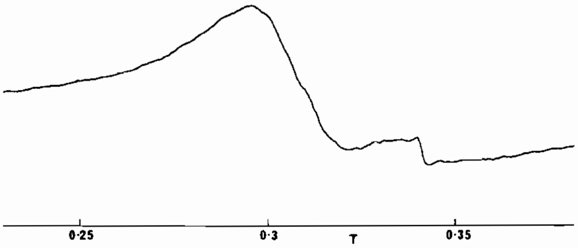

Fig. 3. X-band (9.509 GHz) spectrum of the solid obtained from FA and $K_2Cr_2O_7$ at pH 2.06.

increase in the solution pH (e.g. for the solution yielding the results shown in Fig. 2a the pH changed from an initial value of 3.15 to 3.48 after one hour). At even lower pH values a precipitate was formed. The EPR spectrum of the supernatant liquid consisted of a very broad band in the $g = 2$ region, typical of Cr(III), as the major component, with a very small, sharp Cr(V) signal superimposed on the Cr(III) band. The solid, after triple washing with 0.2 M hydrochloric acid and drying *in vacuo* gave a similar EPR spectrum (Fig. 3), again showing that the product of the reaction between Cr(VI) and FA at $\text{pH} < 3$ was mainly Cr(III).

The results of our studies show that the fulvic acid component of soil humic material resembles the humic acid fraction in its ability to convert Cr(VI) to water-soluble Cr(V). The Cr(V)/FA system gives a much simpler EPR spectrum than its HA counterpart. The conversion takes place over a wider pH range than was found [7] to be the case for the Cr(VI)/HA interaction, though, as with HA, conversion to Cr(V) is favoured by mildly acid conditions.

Fulvic acids occur widely in solution state (peat-bog water, rivers, estuaries, etc) as well as in the solid form in soils. The formation of relatively long-lived Cr(V) by FA and its aqueous solubility over a wide pH range should not be ignored in assessing the ecological consequences of disposing of industrial wastes containing Cr(VI).

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