

Characterization of Humic Acids from Sludge Pond Solids*

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Considerable quantities of organic material, insoluble in common organic solvents, are known to be associated with the inorganic minerals present in oil sands. This insoluble organic matter (IOM) consists of both humic and non-humic components. This organic matter is believed to be partly responsible for the intractability of the sludge. In our previous work we have successfully isolated non-extractable residual organic matter from oil sand tailings using oil phase agglomeration and acid dissolution techniques. In this investigation we have isolated humic acids from a number of samples of mineral solids obtained from Syncrude sludge pond tailings. These solids were obtained from sludge using different experimental conditions such as soxhlet extraction followed by air drying of solids and centrifugation followed by air drying or vacuum drying of solids. Humic matter was extracted from these solids using a mixture of $\text{Na}_4\text{P}_2\text{O}_7$ and NaOH which extracts both humic acids as well as organometallic compounds. Extraction with NaOH yielded humic acids from this composite organic material. The various samples of humic acids isolated were studied using elemental analysis and ^{13}C NMR spectroscopy.

INTRODUCTION

Athabasca oil sand is a complex, variable mixture of bitumen, sand, water and clays. The hot water process used for the extraction of bitumen from oil sands produces large volumes of tailings, consisting mainly of sand and a dispersion of various clay minerals. Some of these clay minerals are associated with significant amounts of insoluble organic matter (IOM).¹⁻⁷ This insoluble organic matter consists of both humic and non-humic components and is believed to be partly responsible for the intractability of the sludge.

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In our previous work we have successfully isolated non-extractable (toluene insoluble) residual organic matter from oil sand tailings using oil phase agglomeration and HCl/HF mineral dissolution techniques.^{4,8} Characterisation of this organic material using elemental analysis and spectroscopic techniques was reported recently.³⁻⁵ Based on those investigations it was suggested that the non-extractable organic material associated with oil sand minerals was mostly humic matter. This conclusion was also supported by the work of Ignasiak et al⁷ who have reported that this organic matter consists of humic and non-humic components containing numerous oxygen functions.

In this investigation we have extracted humic acids from a number of samples of Syncrude sludge pond solids which had been treated under different experimental conditions. The various samples of humic acids isolated were studied using elemental analyses and ¹³C NMR spectroscopy. The results of this study have been compared with the results obtained for the humic acids from oil sands feedstocks.⁹

EXPERIMENTAL METHODS

Materials. The tailings pond sludge was provided by Syncrude Canada Ltd. A list describing the various samples subjected to humic acid extraction is shown in Table I.

Table I. Feedstocks description

Sample ID	Sample Description	Ash (w/w %)	C (w/w %)
UTS	Untreated sludge	-	-
TEODS	Toluene extracted oven dried solids from sludge	94.5	2.6
ODS	Oven dried untreated sludge	85.4	5.3
CWS	Centrifuged wet solids from sludge	-	-
CVDS	Centrifuged vacuum dried solids from sludge	81.7	4.7

Humic Acid Extraction. Samples were first extracted using a mixture of 0.5 N NaOH + 0.1 M Na₄P₂O₇ to isolate composite organic matter consisting of a mixture of humic acids and organometallic compounds. This composite organic matter was then extracted with 0.1 N NaOH to isolate humic acids.

Elemental Analyses. Elemental analyses were performed using standard procedures reported previously.⁹

NMR Measurements. The solid state ¹³C NMR spectra were obtained either at 45.28 MHz or at 75.47 MHz, using a magic angle spinning probe. For all samples a cross polarization technique was used with a contact time of 2-3 ms, and a repetition time of 1 s. Each spectrum was the Fourier transform of 1500-40,000 free induction decay curves.

RESULTS AND DISCUSSION

Humic acids were extracted from a number of Syncrude sludge pond tailings samples that had been pretreated in accordance with the list shown in Table I. In Table II are listed the yield and ash content for each humic acid sample. The yield was calculated as weight percent of the total insoluble

Table II. The yield and ash content of humic acids

Feedstock	Humic Acid Yield (w/w % of IOC*)	Ash Content of Humic Acid (w/w %)
UTS	21.7	8.9
TEODS	18.5	55.3
ODS	18.4	1.6
CWS	15.6	2.8
CVDS	19.7	51.2
Oil sands (Ref. 9)	15.4 ± 9.4	6.8 ± 5.8

* Insoluble organic carbon

organic carbon of the solids in the various samples. The amount of humic acid that could be extracted from various samples did not vary significantly (18.8±2%). Also, the amount of humic acids extracted from sludge samples compared with that extracted from oil sand feedstocks. This suggests that no significant quantities of humic matter could have been formed during oil sands processing or sludge storage and that the humic acids extracted from sludge solids could have been part of the humic matter associated with clay minerals of oil sands feedstock.

Ash content of the humic acid samples varied considerably. Humic acid samples extracted from TEODS and CVDS had the highest ash content of all the samples.

Elemental Analyses. The elemental analyses data are listed in Table III and can be summarized as follows:

Table III. Elemental Analyses of Humic Acids (w/w % dry, ash free)

Feedstock	Elemental Analysis					Atomic Ratios	
	C	H	N	S	O*	H:C	O:C
UTS	71.3	6.8	1.2	2.8	17.9	1.14	0.19
TEODS	56.3	5.8	0.8	1.3	35.8	1.24	0.48
ODS	75.4	7.5	1.0	4.1	12.0	1.19	0.12
CWS	66.6	4.5	1.5	1.6	25.8	0.81	0.29
CVDS	66.2	6.9	1.7	2.8	22.4	1.25	0.25
Oil Sands (Ref. 9)	66±1.5	5.2±0.7	1.2±0.2	3.1±0.6	24.5±1.7	0.95±0.1	0.28±0.02

1. There was more variation in the elemental composition of humic acids extracted from Syncrude sludge pond tailings than those extracted from the oil sand samples reported previously.⁹ This suggests that either the treatment of the samples of Syncrude sludge pond tailings has altered the humic matter eg. by oxidation or that the proportion of humic matter components extracted by a solution of Na₄P₂O₇/NaOH varies from sample to sample.

2. The average elemental composition of these samples resemble those derived from coal and oil sand rather than those extracted from soil or marine sediments.⁹⁻¹¹

¹³C NMR spectra. The solid state ¹³C NMR spectra of the five humic acid samples extracted in this investigation are shown in Figure 1. The main features of these spectra are summarized below:

1. The NMR spectra of the samples derived from UTS and ODS have better spectral resolution than those of the other three samples. However, the spectral resolution does not appear to depend on the ash content of the samples.
2. None of the spectra showed any noticeable resonance in the carbohydrate region.
3. Only samples derived from ODS and CVDS had well defined resonances in the carboxylic region. Non-uniform distribution of carboxylic carbon could be due to the difficulties associated with its detection in these types of samples.
4. The aromaticities (f_a) of the five humic acid samples ranged from 0.47 to 0.62. These values were comparable with previously reported values for humic matter fractions from oil sands.^{4,5,9} However, these values are considerably higher than those reported for soil or aquatic humic acids. The higher values are closer to those reported for humic acids from victorian coal lithotypes.

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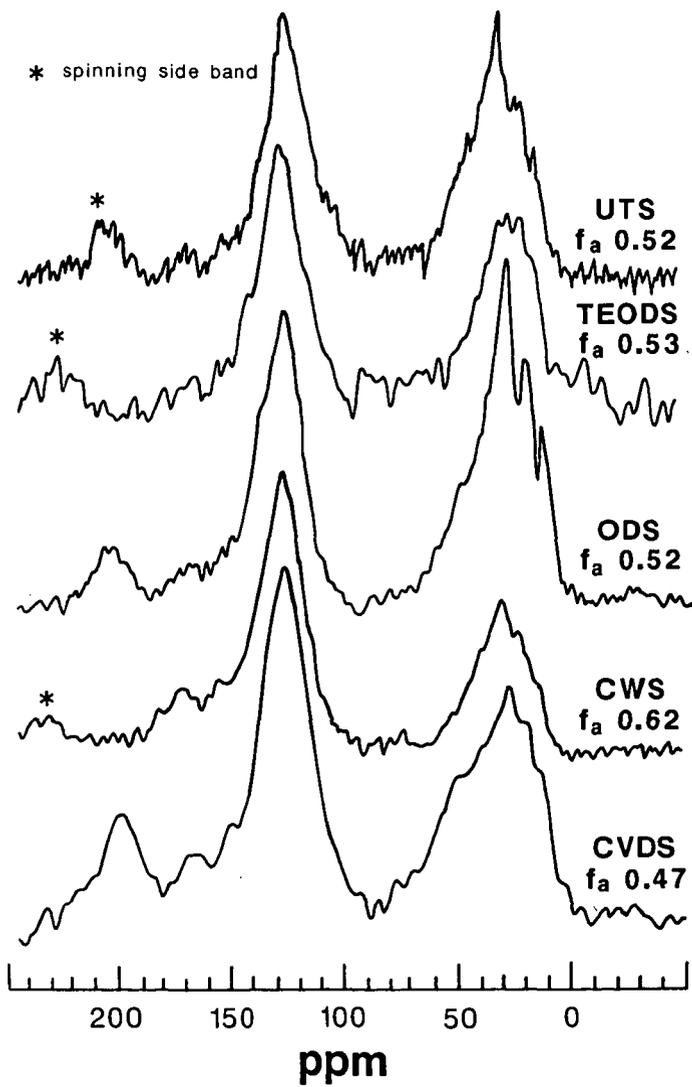


Figure 1. CP/MAS - ¹³C NMR spectra of humic acids