Sulfur Forms in Fulvic Acids of Anaerobically Digested Sewage Sludge

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ABSTRACT

Analytical methods were employed to characterize 80 to 90% of the sulfur (S) in two fulvic acids extracted from anaerobically digested sewage sludge. The majority of the sulfur (69%) was present as organic ester sulfate with smaller contributions from LAS-type detergents, amino acids, and inorganic sulfates. Of the ester sulfate, between 20 and 30% was identified as sulfate esters of fatty alcohols, presumably of detergent origin, and about 5% was accounted for sulfated acidic polysaccharides. It was concluded that because of the ubiquitous distribution of sulfate esters (7.99±0.11 in A,%;3.09±0.08 in B1,%), the disposal of anaerobically digested sewage sludge should not alter drastically the character of sulfur in natural soil and water systems. Perhaps of greater concern would be the contribution of carbon-bonded sulfur from LAS-type detergents(0.6348±0.0164 in A,%;0.4316±0.0020 in B1,%), which have no common natural analogs.

Key words: Ester sulfate , sulfate polysaccharides, surfactants,LAS, fulvic acid .

INTRODUCTION

The fulvic acid fraction of anaerobically digested sewage sludge is the class of extractable, water-soluble, organic compounds that should figure most importantly in the aqueous environmental chemistry of sludge when it is disposed of on land or in natural waters. The analytical properties of fulvic acid (FA) extracted from anaerobically digested sewage sludge have been studied (Sposito *et al.*, 1976, 1978;l Holtzclaw and Sposito, 1978, 1979; Holtzclaw *et al.*, 1980) with the primary objective of comparing them in detail to the well-established characteristics of FA extracted from naturally occurring soil organic matter (Schnitzer and Khan, 1972). This kind of comparative investigation should help bring into sharp focus the purely anthropogenic aspects of the chemical transformations of anaerobically digested sewage sludge which occur in soil or natural water environments.

One of the most striking differences, between sludge-derived FA and either soil-derived or aquatic FA, is in the content of sulfur (Sposito *et al.*, 1976). A typical soil FA, for example, will contain < 2% S (water-and ash-free basis), whereas a representative sludge FA will contain from 4 to 15% S (Sposito *et al.*, 1976; Schnitzer and Khan, 1972). The cause of this large difference is partially understood. Sludge-derived FA has a larger content of S-containing amino acids than soil-derived FA (Holtzclaw *et al.*,

1980) but these constituents seem to account for about 5% or less of the total S. Perhaps more significant are the anionic surfactants in sludge FA (Holtzclaw and Sposito, 1978). These components, which are likely to be either linear alkyl benzene sulfonates (LAS) or sulfate esters of fatty alcohols, such as sodium lauryl sulfate (NaLS) and sodium myristyl sulfate (NaMS), represent anthropogenic compounds that are unique to sludge-derived FA (Sposito *et al.*, 1976; Holtzclaw and Sposito, 1978). Previous work has shown that unaltered LAS-type surfactants amount to approximately 5% of the dry, ash-free mass of sludge FA and that they contribute up to 10% of the total sulfur content (Holtzclaw and Sposito, 1978). Presumably the relatively stable degradation products of these surfactant compounds, e.g.; alkyl carboxy benzene sulfonic acids (Leidner *et al.*, 1976) also are present in sludge FA along with both unaltered and degraded ester sulfate detergents. These compounds , as a whole, may contribute significantly to the sulfur content of sludge FA. Another important possible contributor is the large carbohydrate fraction of sludge FA (Sposito *et al.*, 1976, 1978; Holtzclaw *et al.*, 1980). Since carbohydrates quite commonly occur as sulfate esters (Freney, 1967) those in sludge FA may add to the organic ester sulfate component beyond what comes from detergents.

Although sulfur is an essential element for plant growth, the environmental effect of the organic compounds in sewage sludge which contain still may be adverse, especially if these compounds are not degraded rapidly by microbial organisms. Some evidence exist for the persistence of anionic surfactants in the soil environment under certain conditions, e.g., low soil pH value, high water content, and protection by the soil adsorption complex (Acher and Yaron, 1977; Inoue *et al.*, 1978; Schaumberg *et al.*, 1980; Sposito *et al.*, 1982). Thus it is important to establish the significance of these materials in sludge FA as well as that of the other components of the organic sulfur fraction. In this paper, the sulfur in two representative fluvic acids extracted from anaerobically digested municipal sewage sludge is characterized quantitatively by methods which should be of general utility in studies of fluvic acid chemistry. The principal objective of the present investigation was to determine how much of the sulfur in sludge-derived FA can be attributed collectively to organic and inorganic sulfates, S-containing amino acids, and anionic surfactants.

MATERIALS AND METHODS

Fulvic Acids Extraction:-

Fulvic acid fractions of two representative, anaerobically digested sewage sludges were chosen for study on the basis of their significantly different sulfur contents (Sposito *et al.*, 1976). The sludge materials were collected from the drying beds at the Kafr El-Dawar City, Behera Governorate. The method of extraction and purification of the fulvic acids has been described by Holtzclaw *et al.*, (1976). Fulvic acid A is characterized by a sulfur content of approximately 12% (water-and ash-free basis); fulvic acid B1 contains about 4.5% S (Sposito *et al.*, 1976). After purification, both FA samples were stored in lyophilized form over P_2O_5 under vacuum prior to their use in experiments.

Sulfate Analysis:-

The total organic sulfate and the inorganic sulfate content of the FA samples were determined directly, whereas the organic sulfate content was obtained by difference between total and inorganic sulfate.

The total sulfate content in FA was determined according to the following procedure. A weighed, 50 mg FA sample was transferred to a 50 ml beaker and dissolved in 4 ml of an acid mixture comprising a 4:2:1 ratio (by volume) hydroiodic acid (sp gr = 1.5), formic acid (90%), hypophosphorous acid (50%). This acid mixture has been used to cleave organic sulfate esters and, subsequently, under reflux, to reduce the resulting sulfate compounds to hydrogen sulfide, which then may be analyzed directly (Johnson and Nishita, 1952; Freney, 1961; Tabatabai and Bremner, 1972).

The reducing acid-FA mixture was warmed slightly on a hot plate, and 10 ml of 10% $BaCl_2$ was added. The solution was then allowed to cool and the resulting precipitate was filtered using Whatman No. 42 filter paper. The precipitate consisted of $BaSO_4$ and some oily, noncrystalline materials which were assumed to be organic-barium complexes which proved to be soluble in 1 *N* HCl. The precipitate was washed with 1 *N* HCl to remove these complexes and excess barium. The washings were monitored by adding a few drops of H_2SO_4. When no precipitation was detected in the filtrate, three additional washings were done and the precipitate was dried. The precipitate then was placed in a porcelain crucible and ashed at 750°C for four hours in a muffle furnace. After ashing, the samples were placed ,while still warm, in a vacuum desiccators over P_2O_5. The mass of the dried $BaSO_4$ precipitate represented the sum of organic ester sulfate and inorganic sulfate present in the original FA sample.

Analysis of the inorganic sulfate of the FA was accomplished as follows. A 50 mg sample was dissolved in 25 ml of water. The solution was passed at approximately 1 ml/min through a 1.25-i.d. by 40 cm column containing a Bio-Rad AG-3X 4A anion exchange resin (weakly basic, chloride form, 20-50 mesh). Subsequently, the column was washed with 200 ml of deionized water. The adsorbed sulfate then was eluted with 250 ml of 0.5*N* NaOH. This method was developed because previous experiments (Holtzclaw and Sposito, 1978) had shown that anionic surfactants of the LAS type were adsorbed very strongly by this resin. The only effective eluant for the desorption of the surfactants being a 1:1 methanol-benzene mixture in a *0.04N* KOH background. An alkaline solution alone would not desorb the surfactants, but standard inorganic sulfate was shown to be completely desorbed by *0.5N* NaOH. Since standard NaLS was found not to be adsorbed by the resin, any organic ester sulfate should have passed directly through the column with the first aqueous washings. This technique is effective for separating the inorganic sulfate from anionic surfactant compounds and organic ester sulfates. The eluted sulfate solution was adjusted to pH 2.5 with *1N* HCl, warmed, and treated with 10 ml of 10% $BaCl_2$. The resulting precipitate was filtered, wash, ashed, and weighed as described previously. The total ester sulfate could be calculated by subtracting the contribution of inorganic sulfate from the measured total sulfate.

Anionic Surfactants:-

Unaltered (i.e., non-biodegraded) LAS type surfactant was determined in the FA samples by the method of Holtzclaw and Sposito (1978). The content of unaltered plus partially degraded LAS type surfactant was measured by the following method which was suggested by Takayama (1957) who used $BaCl_2$ to separate LAS type surfactants from detergent mixtures. A 50 mg sample of FA was warmed on a hot plate in 4 ml of the reducing acid mixture, described above, until dissolution was complete. The beaker was covered with a watch glass and the solution was refluxed for 0.5 hour. The watch glass was then removed and heating continued until approximately 2 ml of solution remained. This procedure was used to remove inorganic and organic ester sulfate by reduction to H_2S (Johnson and Nishita, 1952; Freney, 1961; Tabatabai and Bremner, 1972). After cooling, the pH of the solution was adjusted to 7.0 with concentrated NH_4OH followed by *1N* NH_4OH. This pH adjustment was necessary because the Ba salts of anionic surfactants proved to be somewhat soluble at acidic pH values. Preliminary experiments with standard LAS showed that no loss of reacted material occurred at pH 7.0. In addition, a blank solution adjusted to pH 7.0 with NH_4OH gave no precipitate when $BaCl_2$ was added. The neutral solution was warmed, and 10 ml of 10% $BaCl_2$ were added slowly with stirring and heating. After the solution was brought to a boil, it was allowed to cool and stand overnight in a covered beaker. The barium salts of the surfactants were then isolated by filtration using Whatman No. 42 filter paper. The precipitate was washed with H_2O and adjusted to pH 7.0 with dilute NH_4OH. The washings were checked periodically with a few drops of H_2SO_4 to test for complete removal of excess Ba. When barium was no longer detected in the washing, the precipitate was washed three more times and allowed to dry. The sample was then ashed, as previously described, to determine the amount of sulfur contained in both unaltered and altered LAS.

A standard LAS type anionic surfactant in the hydrogen form gave no residue when ashed. However, when it was treated with $BaCl_2$, washed as above and ashed, the ash in the form of $BaSO_4$ accounted for all of the sulfur present in the initial sample.

The determination of anionic surfactants of the NaLS type was accomplished by quantitative gas chromatographic analysis of the organic fraction resulting from acid hydrolysis of FA sample. This procedure was developed based on the fact that sulfate esters are easily hydrolyzed in acid media (March, 1977). Cross (1977) has indicated that NaLS is 98% hydrolyzed by *1N* HCl at 100°C after 7 hours, although quantitative recovery of the residual fatty alcohols was not demonstrated. When standard NaLS was hydrolyzed in HCl, the samples contain volatile reaction products, as evidenced by the development of pressure in the sealed reaction tubes. Chromatograms from these samples showed peaks with relatively shorter retention times as well as peaks for the C_{12} and C_{14} alcohols anticipated. A series of timed hydrolysis experiments showed the growth of the earlier peaks with time and the concomitant decrease of the peaks for the C_{12} and C_{14} species. On the basis of the lower nucleophilicity of sulfate (March, 1977), H_2SO_4 was considered as an alternative reagent for the hydrolysis. A repeat of the timed hydrolysis experiments using H_2SO_4 confirmed the hypothesis regarding the effect of chloride. Essentially 100% recovery of standard material was obtained with hydrolysis using H_2SO.

Triplicate FA samples weighing 0.125 to 0.250 g were placed in clean dry acid-washed screw-capped tubes equipped with teflon cap liners. A glass boiling bead and 1.0 ml of a 5% (v / v) solution of ultra pure H_2SO_4 in H_2O were added. The samples were refluxed for 2 hours at 105°C in a small sand bath and then were allowed to cool to room temperature. The pH was made basic by the addition of KOH(0.04*N*), and the samples were extracted with 2.0 ml diethyl ether, mixed thoroughly on a vortex mixer, and centrifuged for 10 min at 5,000 rpm to obtain adequate phase separation. The ether phase was removed, and 10 µ liter were injected directly into a Varian model 2700 dual-column GLC equipped with flame ionization detectors. The columns were 100-cm stainless steel (0.125 i.d.), packed with 20% apiezon L on 100/120 mesh chromosorb W (AW DMCS). Nitrogen carrier gas was used at a flow rate of 24 ml/min measured at room temperature. Injector and detector temperatures were both at 300°C. The separation was performed with a step-wise temperature program from 80° to 260° at 5°C/30 sec. The final temperature was maintained for 12 min. Identifications were made on the basis of co-chromatography with quantitative alcohol standards. Concentrations were determined by comparison of peak areas to that of 1-octanol added as an internal standard.

This procedure was checked using 5 mg samples of standard U.S.P grade NaLS and was found to be quantitative and reproducible. Timed hydrolysis showed that a 0.5 hour reaction time gave the same results as 8 hours. Two hours was chosen as a convenient and reproducible reaction time.

Carbohydrate Sulfate Esters:-

The procedure of Scott (1955) was adapted for acidic mucopolysaccharides in FA. A sample of 100 mg was placed in a 250 ml beaker and dissolved with stirring in 100 ml of deionized water and the pH of the solution was adjusted to 0.8 using reagent grade HCl. Five milliliters of 2.5% cetyltrimethyl-ammonium bromide was added to the sample solution. The solution was then covered, allowed to stand at approximately 4°C for 18 hours, allowed to warm to room temperature, transferred to 40 ml polyethylene centrifuge tubes, and centrifuged for 15 min at 2,000 g. The supernatant liquid was decanted, and the precipitate was washed twice with deionized water and then dissolved in a few milliliters of concentrated HCl. The resulting solution was transferred quantitatively to a 100 ml round-bottom flask, diluted to approximately *6N* (total volume approximately 25 ml), and refluxed for 18 hours using a Frederick condenser. The solution was allowed to cool, and then 10 ml of $BaCl_2$ solution were added, the resulting $BaSO_4$ precipitate isolated by using Whatman No. 42 filter paper. The precipitate was washed with HCl and deionized water, then analyzed as described previously.

RESULTS AND DISCUSSION

Table (1) shows the percentage of total S, LAS-type surfactant S, amino acid S, ester sulfate S, and inorganic sulfate S determined in fulvic acids A and B . The S percentage contributed by partially degraded LAS type compounds was calculated as the difference between the total S percentage contributed by LAS type compounds and the S percentage contributed by unaltered LAS. Ester sulfate S was calculated as the difference between total sulfate S and inorganic sulfate S. As indicated in Table (2), hydrolysable ester sulfate S accounted for 69% of the total sulfur in both FA samples. This result is in agreement with organic ester sulfate data for soil FA (Freney, 1961; Freney *et al.*, 1969, 1971; El-Sayed, 2002) and Peat FA (Casagrande *et al.*, 1980; El-Sayed, 1998), despite the much lower total S content of these other humic substances. Evidently, the fact that sulfate esters are widespread in nature, occurring in structural components of both plants and animals and in their excretion products, is the principal cause of this similarity in the distribution of organic sulfur in FA fractions extracted from very different organic materials.

The percentage of carbon-bonded S given in Table (2) is significant since it includes primarily the LAS-type surfactants. This particular contribution would not be present in soil or aquatic FA derived from natural organic matter, in which amino acids would be the principal origin of carbon-bonded S.

The nonhydrolyzable S (Table 2) is believed to be a mixture of carbon-bonded organic S and inorganic S. The latter component can be important because of the anaerobic conditions under which the FA fractions were produced; anaerobically digested sludges have been shown to contain about one-fourth of their total S in the form of inorganic nonsulfate S (Sommers *et al.*, 1977; El-Sayed, 2005). Thus at least a portion of the unhydrolyzed S should be present as sulfides and other partially reduced inorganic forms of sulfur.

Tables (3 and 4) present data relating to the nature of the ester sulfate in fulvic acids A and B1. Table (3) shows that unaltered and/or partially degraded NaLS and NaMS surfactants contributed between one-fifth and one-third of the total ester sulfate in the FA samples. This large portion of surfactant sulfates and the liability of the ester sulfate linkage makes sulfate exchange via trans esterification of other organic material in sludge FA is likely high. Thus, detergent-derived sulfate could be bound by various hydroxyl groups in the FA structure. In particular, the carbohydrates, which have been shown to be an important constituent of sludge-derived FA (Sposito *et al.*, 1978; Holtzclaw *et al.*, 1980; El-Sayed, 1995 a and b; abdel-Aziz *et al.*, 2003), might bind detergent-derived sulfate in this fashion. Table (4) indicates that relatively small percentages of the ester sulfate in sludge FA are accounted for by acidic carbohydrates. However, these data perhaps should be regarded as minimum values for the contribution of sulfated polysaccharides for two reasons. First, only "loosely held" carbohydrates are precipitated in the analytical method used. It is possible that much of the carbohydrate is tightly bound into the FA structure and that strong acid hydrolysis does not liberate all of it (Linhares and Martin, 1979; El-Sayed, 1999 a & b). Second, the technique employed measures only acidic polysaccharides. In view of the fact that sludge FA contains high levels of neutral sugars (Holtzclaw *et al.*, 1980; El-Sayed, 2003 and 2004) which also can bind sulfate. It is not likely that all of the carbohydrate-bonded sulfur is detected by the analytical procedure used.

CONCLUSIONS

Chemical analysis of sulfur in fulvic acid extracted from anaerobically digested sewage sludge has satisfactorily characterized some of the forms in which it occurs. The largest fraction occurs as organic sulfate esters. Other forms include sulfur-containing amino acids, undegraded and partially degraded LAS-type detergents, sulfonated acidic polysaccharides, and inorganic sulfate. The relatively small fraction of uncharacterized sulfur is hypothesized to comprise miscellaneous carbon-bonded sulfur and inorganic nonsulfate compounds.

The fact that organic sulfate ester accounts for the largest fraction of the sulfur in anaerobically digested sludge FA is analogous to the situation in natural organic matter. However, the relatively higher percentage of sulfur in sludge-derived fulvic acids is unique. Approximately 25% of the ester sulfate appears to be sodium lauryl sulfate and related detergents. Another 5% is accounted for sulfated acidic polysaccharides. The organic portion of the other 70% remains uncharacterized. In view of the relative ease of hydrolysis of sulfate esters and the demonstrated high levels of carbohydrates in the samples, NaLS-type detergents may be responsible for at least a portion of the uncharacterized sulfate via transesterification of hydroxyl groups in carbohydrate molecules incorporated into the FA structure.

Because of the ubiquitous distribution of sulfate esters, it appears that the disposal of anaerobically digested sewage sludge should not drastically alter the character of sulfur in soil and natural water systems. Perhaps of greater concern are the levels of carbon-bonded sulfonic acid groups in the anionic surfactant component of sludge FA, which have no commonly occurring natural analogs .

Table (1): Percentage of sulfur contributed by surfactant, amino acid, ester, and inorganic fractions of 2 sludge-derived fulvic acids (water- and ash – free basis: A and B_1)

Fulvic acid	% Sulfur	
	A	B_1
Total sulfur[(a)]	11.56 ± 0.95	4.46 ± 0.65
LAS-type surfactant		
Unaltered LAS[(b)]	0.6348 ± 0.0164	0.4316 ± 0.0020
Altered LAS	0.1751 ± 0.0114	0.0983 ± 0.0093
Sulfur-containing amino acids[(c)]		
Methionine	0.0549 ± 0.0041	0.036 ± 0.0036
Taurine	0.0051[(d)]	Trace[(d)]
Cysteic acid	0.0171 ± 0.0003	0.0741[(d)]
Half-cystine	0.0024 ± 0.0004	0.1450 ± 0.0021
Ester sulfate	7.99 ± 0.11	3.09 ± 0.08
Inorganic sulfate	0.23 ± 0.03	0.30 ± 0.04

(a) Sposito *et al.* (1976) method. (b) Holtzclaw and Sposito (1978) method
(c) Holtzclaw *et al.* (1980) method. (d) One determination only.

Table (2): Distribution of sulfur-containing constituents in sludge-derived fulvic acids(A and B_1)

Fulvic acid	% of total Sulfur	
	A	B_1
Hydrolyzable ester sulfate-S	69.09	69.29
Measured carbon-bonded S[(a)]	7.69	17.60
Inorganic SO_4-S	1.99	6.82
Total characterized-S	78.77	93.71
Unknown-S	21.23	6.29

(a) Sum of previously measured carbon-bonded S species (Holtzclaw and Sposito, 1978 method; Holtzclaw *et al.*, 1980 method).

Table (3): Content of NaLS or NaMS in sludge-derived fulvic acids (water–and ash – free basis)

Fulvic acid	Carbon chain length	Average (µg) ROH/mg FA	Average (µg) NaLS or NaMS/mg FA	% NaLS or NaMS in FA	% NaLS or NaMS sulfate of total ester sulfate
A	**C_{12}**	**24.93 ± 0.57**	**38.58 ± 0.88**	**3.86**	**16.10**
	C_{14}	**11.44 ± 0.73**	**16.89 ± 1.08**	**1.69**	**6.42**
B_1	**C_{12}**	**13.69 ± 0.93**	**21.18 ± 1.44**	**2.12**	**22.83**
	C_{14}	**5.16 ± 0.55**	**7.62 ± 0.82**	**0.76**	**7.45**

Table (4): Relationship of sulfur in the acidic sugar fraction to total sulfur and ester sulfur

Fulvic acid	Total S (%)	Ester SO_4-S (%) of total S	% Acidic Sugar-S of total S	% Acidic Sugar-S of ester SO_4-S
A	11.56 ± 0.95	69.09	3.89	5.63
B_1	4.46 ± 0.65	69.29	4.71	6.80

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الملخص العربي

صور الكبريت فى أحماض الفلفيك لحمأة مياه المجاري المهضومة لاهوائية

سعيد عباس محمد السيد

كلية الزراعة – جامعة الأزهر بأسيوط قسم علوم الأراضي والمياه

أوضحت النتائج باستعمال مجموعة متنوعة من طرق التحليل لمعرفة صور الكبريت (S) ما يلي : – وجود نماذج من أحماض الفلفيك المستخلصة من حمأة مياه المجاري اللاهوائية المهضومة بنسبة نتراوح ما بين ٨٠% إلى ٩٠% .– أحماض الفلفيك المستخلص من التربة و Peat غالبيتها تمثل نسبة ٦٩% من الكبريت (S) على صورة استرات كبريتات عضوية ، أحماض أمينية ، وكبريتات غير عضوية ، قليل من LAS النقية .– تراوحت إستر الكبريتات ما بين ٢٠% إلى ٣٠% والتي تشابه مثيلاتها في الكحولات الدهنية ، ٥% من الكبريتات الحمضية لعديدة السكريات .– مادة الكبريت الكلية موزعة كإستر كبريتات .– يجب التخلص من حمأة مياه المجاري اللاهوائية المهضومة حتى لا تؤثر على نظام التربة والمياه في الطبيعة .– توجد نسبة كبيرة من رابطة الكربون بالكبريت ، وتوجد LAS نقية والتي لا نظير لها في الطبيعة .