

Coal Humic Substances for Pollution Control in the Synthetic Fuels Industry

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INTRODUCTION

Large quantities of by-product wastewater are associated with many of the major processes employed for synthetic fuels manufacture (1). Typical examples are water used to scrub dust, tar, and soluble organic compounds from the product of coal gasification and by-product water from the retorting of oil shale. Depending upon the source, these waters may contain substantial quantities of phenols, dissolved nitrogenous organic compounds, polycyclic aromatic hydrocarbons, biodegradable organics exerting a biological oxygen demand, heavy metals, ammonia, and other solutes. As both potentially valuable by-products and pollutants, the removal of these substances from by-product water is required.

It is imperative that economics and practicality be given the utmost consideration in the development of processes for the treatment of large quantities of by-product water from synthetic fuels manufacture because of the enormous quantities of water involved in a commercial synthetic fuels industry. Water treatment systems requiring expensive synthetic chemicals, elaborate apparatus, and intricate operations cannot be employed economically on a commercial scale. These considerations tend to exclude processes depending upon the use of large quantities of synthetic ion exchange resins, synthetic flocculents, and similarly expensive chemicals. Furthermore, for economic reasons and to avoid disposal of excessive amounts of waste chemicals, recyclable chemicals or those with a fuel value must be employed wherever possible.

This research has examined the uses of coal humic substances (CHS) for the treatment of by-product water. These materials meet the criteria of ready availability, low cost, and processing simplicity. In addition, similar substances can be isolated from oil shale, and it is possible that these materials may find uses in pollution control. The preparation, properties, and selected applications of these materials to pollution control are discussed in this report.

PREPARATION AND PROPERTIES OF COAL HUMIC SUBSTANCES

Humic substances are degradation resistant organic compounds derived from vegetable matter. These materials participate significantly in the environmental chemistry of water and soil (2). Humic substances are divided into three main categories based upon extraction with base and subsequent treatment of the extract with mineral acid: (a) a non-extractable residue called *humin*, (b) *humic acid* precipitated when the extract is acidified, and (c) *fulvic acid* remaining in the acidified solution. Additional details regarding the significance and properties of these fractions are to be found in the literature (3).

Humic substances may be prepared by the partial oxidation and base extraction of coal. In this work the general term, *coal humic substances* (CHS) is employed to describe these materials. The major categories of coal humic substances considered herein are *coal humic acids* (CHA), water-soluble coal humates (e.g., the sodium salt of coal humic acid), and water-insoluble coal humates (particularly the calcium salt of coal humic acid). Numerous works have been published dealing with coal humic substances. These are summarized in two publications (4,5) dealing with the subject.

Coal humic substances are formed as intermediate steps in the partial oxidation of coal under moist conditions. This occurs by way of the general sequence shown in Figure 1. Figure 2 shows a hypothetical "molecule" of coal humic acid. It should not be taken as an exact, or even typical structure, but rather to illustrate the main structural and functional characteristics of this material.

Coal humic acids and their humate salts have a number of properties which make them potentially useful for wastewater treatment. These properties, and their potential applications to wastewater treatment, are the following:

1. Coal humates react with H^+ ion in solution. Therefore, solutions of soluble coal humates or suspensions of insoluble coal humates may be employed to neutralize mineral acid in excessively acidic wastewaters, or to sorb acid gases, such as SO_2 , from gas streams.
2. Coal humic acids and most coal humates (other than alkali metal, magnesium, and ammonium humates) are water-insoluble. This provides a solid phase into which impurities may be partitioned and removed from wastewater and enables removal of humic substances from water that has been treated with these materials. Suspended solids in wastewater are entrained and removed by the precipitation of humates.
3. Heavy metal ions strongly chelated by coal humic substances may be removed by precipitation of the chelates or sorption of the chelates by a solid sorbent.
4. Some classes of organic compounds are sorbed by humic acids and insoluble coal humates enabling their removal from water.

5. Coal humic acids behave as flocculents in the precipitation of inorganic compounds, such as metal hydroxides or carbonates, produced in water treatment.
6. Solutions of coal humates foam strongly, leading to potential applications in froth flotation treatment of water.

EXPERIMENTAL

Coal humic acid used in these studies was prepared by nitric acid oxidation of Wyoming Wodak Amax sub-bituminous coal. Each batch consisted of 100 g of pulverized coal slurried to a thick paste with water. A volume of con. nitric acid equal to the volume of the coal slurry was added in 10 small batches, with stirring, over a 1-hour period. *Because of the evolution of NO₂ gas and the possibility of violent ejection of the material from the container, this operation must be performed cautiously in a hood with proper shielding.* The mixture was allowed to stand for 2 hours after the addition of all nitric acid. It was then washed with approximately 3 times the volume of residual solid by each of the following in sequence: (1) 3 separate batches of distilled water, (2) 1 batch of con. HCl for iron extraction, and (3) 3 separate batches of distilled water. The humic and fulvic acid fractions were then dissolved in 500 ml of 1.0 M NaOH, the solid residues were removed by centrifugation, and coal humic acid precipitated at pH 3 with con. HCl. After settling overnight, the humic acids were removed by centrifugation and washed twice with 1×10^{-3} M HCl, followed by centrifugation after each washing.

The removal of organic compounds labeled with radioactive carbon-14 from oil shale retort water was followed with a Beckman Instruments Model LS-9000 liquid scintillation spectrometer. Aqueous samples (0.5 - 1.0 ml) were counted in 12 ml of Dimilume-30 (Packard Inst. Corp.). All samples were counted for a sufficient time to achieve a 2-sigma statistical counting error of 1% or less.

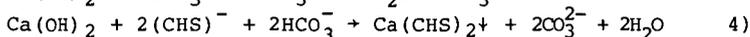
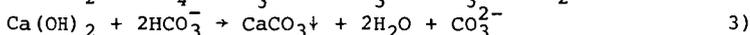
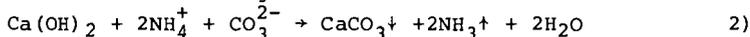
The predominant cation in the oil shale retort water studied is NH_4^+ ion (271 meq/l) and the predominant anion is HCO_3^- (247 meq/l). Approximately 75-ml quantities of this water were dosed with less than 1 mg/l of ^{14}C -labeled compound whose removal was to be studied. A 50-ml portion of the spiked retort water was removed and 1.0 g of coal humic acid gel added to this portion, dissolving to form a black coal humate solution in the basic medium. Three 8-ml portions of labeled retort water (without added humic acid) and three 8-ml portions containing added humic acid were measured into 15-ml centrifuge tubes. Exactly 206 mg of solid $\text{Ca}(\text{OH})_2$, 10 percent greater than that required stoichiometrically to remove all HCO_3^- and CO_3^{2-} , was added to each tube followed by thorough mechanical agitation. A voluminous precipitate of CaCO_3 , darkened by the presence of calcium humate in those samples containing dissolved coal humic substance, formed immediately. The samples were centrifuged for 20 minutes at 2000 rpm, 0.5 or 1.0 ml aliquots of supernatant were withdrawn, and these were subjected to radioassay by liquid scintillation counting. Comparison of the supernatant to the untreated solution enabled calculation of the degree of removal of the spiked compound.

RESULTS AND DISCUSSION

When coal humic acid is added to shale oil retort water, the reaction,



occurs in which the insoluble coal humic acid, $\text{H}(\text{CHS})$, dissolves in the basic medium, producing coal humate anion, $(\text{CHS})^-$, and turning the water an opaque black color. Addition of $\text{Ca}(\text{OH})_2$ (lime) to the medium containing ammonium, bicarbonate, carbonate, and CHS^- ions causes the following reactions to occur:



The solubility of calcium coal humate is comparable to that of CaCO_3 so that it is necessary to remove the greater part of the bicarbonate and carbonate to ensure essentially complete removal of dissolved $(\text{CHS})^-$. When this is done and the suspension centrifuged, the supernatant liquid is again transparent and indistinguishable from the original retort water prior to the addition of coal humic acid. The precipitate is a heterogeneous dark gray mass consisting of a mixture of $\text{Ca}(\text{CHS})_2$ and CaCO_3 .

Impurities, including organic impurities, may be coprecipitated with CaCO_3 in oil shale retort water treated with lime, or with $\text{Ca}(\text{CHS})_2$ if coal humic acid has been added. This phenomenon is shown in Table 1. Examination of this table shows a wide variation in removal efficiency with compound. Removal of the organic acids is almost certainly as the calcium salt, and removal efficiency should increase with increasing concentration because of solubility product considerations. In all cases the addition of a small quantity of coal humic acid significantly enhances removal. Increased removal of carcinogenic benz(a)pyrene by the addition of coal humic acid is quite significant. By taking out an additional 2/3 of the benz(a)pyrene that simple lime treatment did not remove, coal humic acid could well make the difference between a marginal treatment and adequate removal of this important compound.

It is noted that naphthalene is the second most efficiently removed compound, perhaps indicating that the removal of aromatics increases with increased condensation. Therefore, treatment with lime plus coal humic acid very likely yields efficient removal of polynuclear aromatic compounds and tars.

Coal humates, the salts of coal humic acids, have some uses for by-product water treatment as noted in the Introduction. Fly ash has been investigated as a source of base for the preparation of coal humates, yielding primarily calcium and magnesium humates. Details of this preparation and its potential uses are given in a reference dealing with the subject (5). In addition to providing a source of base, fly ash so treated is less susceptible to leaching and more amenable to disposal in a satisfactory manner.

TABLE 1. Removal of Carbon-14 Labeled Compounds from Oil Shale Retort Water by Treatment with Lime and Lime Plus Coal Humic Acid.

Compound	Percent removal with lime	Percent removal with lime plus coal humic acid
Benz(a)pyrene	97.5	99.2
Naphthalene	50.4	69.2
Phenol	1.28	5.61
Benzoic acid (benzoate anion)	0.00	3.99
Octanoic acid (octanoate anion)	18.7	27.9
KCN (cyanide ion)	5.08	8.74
Carbonate species*	94.4	not measured

* Spiked with ^{14}C -labeled Na_2CO_3 , largely converted to HCO_3^- ion by equilibria in the solution.

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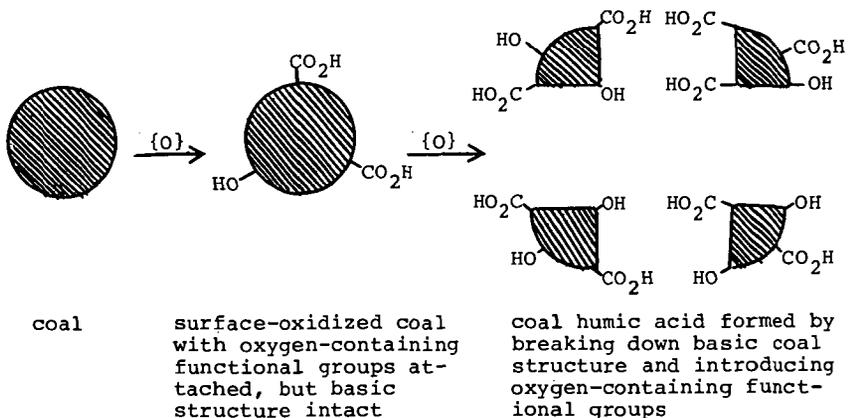


FIGURE 1. Partial oxidation of coal to form surface-oxidized coal and coal humic acid

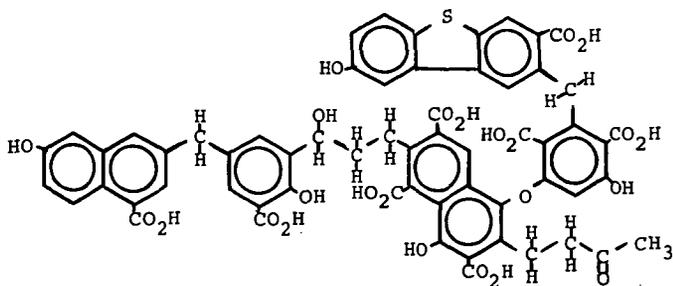


FIGURE 2. Representation of a coal humic acid molecule showing the predominant structural and functional features.