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Characterization of Humic Acids from Kuye San Soil

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Three humic acids, two from uranium bearing coal shale and one from the neighbouring limey shale region, are extracted from soils by dissolution in 0.1 M NaOH followed by acid precipitation. After purification cycles, they are characterized for their elemental composition, contents of inorganic impurities, molecular size distribution and proton exchange capacities. The results are compared with the data of reference and aquatic humic acids characterized under the project MIRAGE II at TUM and also with other literature data. The proton exchange capacity determined by direct titration, is found to be 3.60 and 2.01 meq/g for coal shale and limey shale humic acids, respectively.

Introduction

A wide variety of natural and man-made organic species are present in the environment which can play an important role in the migration of heavy metal ions ($Z \geq 2+$) by complexation in natural aquifer systems.^{1,2} Among natural organics, the most preponderant species are humic and fulvic acids which are polyelectrolytes with high complexation affinity for metal ions in particular with Fe^{3+} , Fe^{2+} , Ca^{2+} and rare earth metal ions present in water. The aquatic humic acid loaded with metal ions forms colloidal particles which are called humic colloids.^{3,4} Such colloids, by their ion exchange property in solution, can also form pseudocolloid of actinide or other toxic metal ions.⁴ An enhancement of migration or retention of heavy metal ions in a given aquifer system, with particular filtration and sorption properties, can thus be affected by humic substances. Since humic substances are structurally similar but have different size distribution and functional group content which depend on their origin,^{5,7} a basic knowledge on the nature of humic and fulvic acids and their complexation behaviour are indispensable in establishing better understanding of such processes.

The present work deals mainly with the characterization of soil humic acids from the coal shale containing uranium deposits and limey shale region around Kuye-San, Korea where prospecting for uranium occurred in the past. The characterization of soil humic acids, KS-T1-HA, KS-T2-HA and KS-T3-HA, is necessary for the determination of complexation constant and other key parameters in the assessment of the migrational behaviour of actinides and other heavy metal ions. Analytical data of the humic acids will also provide an insight into the complexation behaviour with naturally occurring U^{4+} and UO_2^{2+} ions of the region.

Experimental

The humic acids (HA) from the Kuye-San soil are extracted by a procedure similar to that described for the north Illinois soil near Joliet.⁸ They are isolated by alkaline digestion of soil and precipitation with addition of an acid to pH 1. The precipitates are redissolved in 0.1 M NaOH and after addition of 0.2 g NaF/g HA left overnight to remove silicate impurities. By repeated cycles of dissolution (0.1 M NaOH) and precipitation (pH 1 by HCl), the humic acid precipitates are washed with 0.1 M HCl until no Na^+ is detected in the supernatant. The protonated final products are freeze dried and stored in a desiccator under vacuum due to hygroscopic property.

C, H and N contents are analyzed by burning some 25 mg of humic acid in O_2 atmosphere and resulting CO_2 , H_2O and N_2 (reduced from NO_2) gases are analyzed by a heat conductivity measurement with CHN Rapid instrument (Heraeus Co.). The oxygen content in the samples is analyzed by a cracking process which oxidize carbon to CO then further to CO_2 over I_2O_5 , and resulting CO_2 quantified by titration. Sulphur is analyzed by oxidizing the sample in H_2O_2 under O_2 atmosphere and titrating H_2SO_4 acid produced with Ba (ClO_4)₂.

Inorganic impurities in humic acids are determined by neutron activation analysis (NAA), sealing 10 mg sample in 5 mm suprasil quartz tube (Heraeus Co.), and irradiating in the FRM (Forschungsreaktor Munchen) at the position with neutron flux of $2 \times 10^{13} \text{ sec}^{-1} \text{ cm}^{-2}$ and subsequently by gamma spectrometry against Au/Co monostandard.

Experiments for the determination of proton exchange capacity is conducted in an argon inert gas box ($\text{O}_2 \leq 4 \text{ ppb}$) with solutions and chemicals free of O_2 and CO_2 (known to cause interferences). About 10 mg HA weighed to 1.0 μg accuracy is dissolved in 1.00 ml of 0.1 M NaOH (carbonate free, Baker Co.) and diluted to 50 ml with 0.1 M NaClO_4 .

Table 1. Elemental Composition of Humic Acids from Different Origins (in wt.%)

Element	KS-T1-HA(H ⁺)		KS-T2-HA(Na ⁺)		KS-T3-HA(H ⁺)		Aldrich-HA(Na ⁻) [ref. 9]		Aldrich-HA(H ⁺) [ref. 9]		Gohy-573-HA(H ⁺) [ref. 9]		Range [ref. 7]
C	53.85	(54.79)	46.55	(54.41)	54.25	(54.48)	41.72	(48.93)	53.44	(55.23)	55.79	(56.25)	(50-60)
H	4.83	(4.91)	3.20	(3.74)	5.69	(5.71)	4.37	(5.13)	4.34	(4.48)	4.48	(4.52)	(4-6)
N	4.12	(4.20)	2.80	(3.27)	4.76	(4.78)	0.25	(0.29)	0.31	(0.32)	1.68	(1.69)	(2-6)
O	35.08	(35.69)	32.70	(38.22)	34.30	(34.45)	36.93	(43.40)	36.43	(37.64)	35.51	(35.80)	(30-35)
S	0.40	(0.41)	0.31	(0.36)	0.58	(0.59)	1.90	(2.33)	2.25	(2.33)	1.72	(1.73)	(0-2)
Rest	1.72		14.44		0.82		14.83		3.25		0.82		

(): Values normalized to 100% of organic components.

This solution is back (and forward) titrated with 0.1 M HClO₄ (0.1 M NaOH) in 10 μ l alotments using the Dosimat 535 (Metrohm Co.) and pH is measured by a digital pH meter (Knick Co.) and Orion Ross glass electrode.

The molecular size distribution of humic acids is determined by ultrafiltration. In a typical experiment, 6 mg of humic acid is weighted and dissolved in 2.5 ml of 0.01 M NaOH, and diluted to 200 ml with 0.1 M NaClO₄ containing 1×10^{-3} M tris buffer [tris (hydroxymethyl) amino methane, reagent grade, Aldrich Chemical]. The experimental setup consists of a stirring filtration cell with 10 ml volume capacity (Product No. 8010, Amicon Co.) which is connected to the flow-through cell (20 μ l capacity) of a Plasma 40 Emission Spectrometer (Perkin Elmer) to quantify humic acid concentration of the filtrate. The filters of differing poresizes are used in the experiment and they are XM300, YM100, XM50, YM30, YM10, YM5 and YM2 (Amicon Co.). The filters are washed with bidistilled water and 0.1 M NaClO₄ (10^{-3} M tris) solution prior to use. The experiment is run under N₂ gas pressure. The absorbances at 280, 300, 465, 665 nm are monitored continuously to characterize each filtrate. The on-line absorption at 300 nm is recorded as a function of the elution volume. A detailed procedure for the humic acid characterization is given elsewhere.⁹

Results and Discussion

Elemental composition. Elemental compositions (C, H, N, O and S) analyzed for the three humic acids under investigation are given in Table 1. These humic acids are classified as KS-T1-HA (H⁺) and KS-T2-HA(Na⁺) from the coal shale soil and KS-T3-HA (H⁺) from the limey shale soil. KS-T2-HA(Na⁺) is an unpurified Na salt. In addition, the data from the reference humic acid, Aldrich-HA, and the aquatic humic acid, Gohy-575-HA, are also shown for comparison. The data in parenthesis are the composition normalized to 100 wt.% of organic component. The rest (in wt.%) shown at the bottom of Table 1, which is the difference between the total initial weight and the sum of the weight of five elements, represents the sum of all impurities. As a whole all three humic acids have the elemental composition data which fall within the ranges that are given in the literature.⁷ The two purified and protonated humic acids, KS-T1-HA and KS-T3-HA, show elemental contents of C and O comparable to those of other humic acids, whereas H contents are higher, probably due to higher aliphatic groups present in soil humic acids. In comparison to the reference (Aldrich-

Table 2. Atomic Ratio H/C and O/C of Soil Humic Acids

Humic acid	H/C ratio	O/C ratio	Ref.
KS-T1-HA(H ⁺)	1.08 \pm 0.02	0.49 \pm 0.01	[this work]
KS-T3-HA(H ⁺)	1.26 \pm 0.02	0.48 \pm 0.01	[this work]
Aldrich-HA(H ⁺)	0.97 \pm 0.01	0.51 \pm 0.01	[9]
Gohy-573-HA(H ⁺)	0.98 \pm 0.01	0.47 \pm 0.01	[9]
HA(H ⁺)-general*	0.93 \pm 0.12	0.50 \pm 0.03	[11]

* Aquatic humic acid.

HA) and aquatic (Gohy-573) humic acids, these soil humic acids have higher nitrogen content, but is lower in sulphur. Such differences may be explained by their origin which lies in another climatic zone.¹⁰ It can also be noted that KS-T2-HA(Na⁺) data show high impurities contents similar to Aldrich-HA(Na⁺).

The O/C and H/C ratios are useful indicators of the presence of various structures in a humic acid.¹¹ The atomic ratios of H/C and O/C for the present soil humic acids are shown in Table 2 together with data from the aquatic and reference humic acids in the literature.^{9,11} The H/C ratio implies a humic acid structure composed primarily of aromatic rings with carboxyl and quinone functional groups. The presence of aliphatic groups including primary amino groups may increase the ratio somewhat larger than unity. The higher H/C ratio for the soil humic acids maybe explained by an abundance of nitrogen to form amino groups as such. The O/C ratio for two protonated soil humic acids are quite similar to one another and to the data in the literature.^{9,11} Therefore their complexation behaviour with metal ions are probably very similar.

Inorganic Impurities. Inorganic impurities in humic acids are mainly bound metal ions. They are determined by neutron activation analysis. The results for two purified soil humic acids are given in Table 3. The results demonstrate that the purification process is very effective, removing much of the impurities bound to the original humic acid extracts. Besides Fe, which has a high complexation affinity for humic acid, the contents of major elements are substantially reduced, when compared to the Aldrich-HA(Na⁺) data given in the literature.⁹ The contents of inorganic impurities are in general higher in KS-T1-HA than KS-T3-HA, because coal shale of the region is enriched in metals including uranium. In the purified soil humic acids, the total contents of inorganic impurities are much smaller than the proton

Table 3. Inorganic Impurities in Soil Humic Acids Determined by the Neutron Activation Analysis (in $\mu\text{g/g}$)

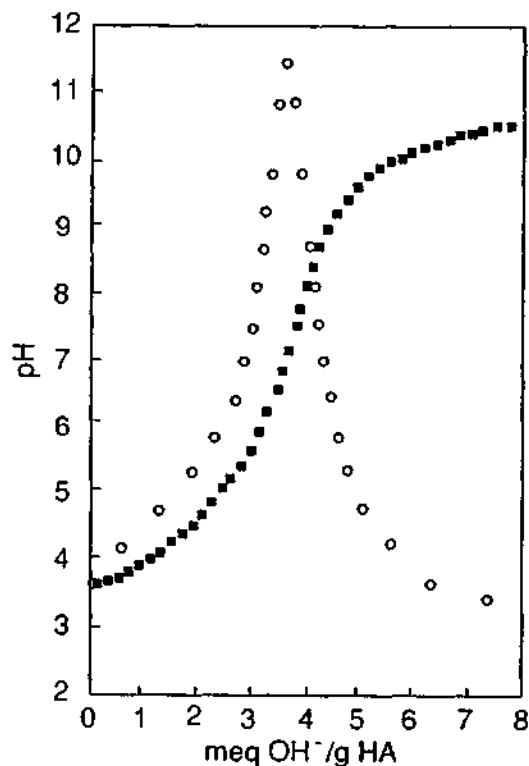
Element	KS-T1-HA	KS-T3-HA
Major		
Ba	249 \pm 20	75.9 \pm 8.9
Co	130 \pm 2	178 \pm 4
Fe	9524 \pm 76	3626 \pm 73
Mo	542 \pm 95	744 \pm 97
Na	3971 \pm 120	1722 \pm 110
U	218 \pm 5	91.6 \pm 6.4
Zn	189 \pm 3	181 \pm 8
Minor		
Ce	21.9 \pm 1.9	10.6 \pm 0.1
Cr	59.0 \pm 1.0	52.6 \pm 1.1
Eu	0.12 \pm 0.01	0.05 \pm 0.01
Hf	0.42 \pm 0.01	0.42 \pm 0.01
La	25.2 \pm 0.1	46.1 \pm 4.0
Tb	0.10 \pm 0.01	0.04 \pm 0.01
Th	26.3 \pm 0.1	16.3 \pm 0.2
Yb	0.24 \pm 0.02	0.11 \pm 0.01

Table 4. Proton Exchange Capacity of Soil Humic Acids Determined by the Direct Acid Titration

Humic acid	Proton exchange capacity (meq/g HA)	Ref.
KS-T1-HA	3.60 \pm 0.30	[this work]
KS-T3-HA	2.01 \pm 0.20	[this work]
Aldrich-HA	5.43 \pm 0.16	[9]
Gohy-573-HA	5.38 \pm 0.20	[9]

exchange capacity of each humic acid, and will not affect the study their complexation with metal ions.

Proton Exchange Capacity. A direct pH titration is known as a simple and accurate method for obtaining the proton exchange capacity (PEC) of humic acids.⁹ The results from pH titration are summarized in Table 4. The PEC of the soil humic acids are somewhat lower than those of the reference and aquatic humic acids. The may be due to the fact that aquatic humic acid has higher numbers of carboxylic and phenolic functional groups which in tern makes it more soluble in water. When the titration is conducted carefully in the absence of CO_2 and O_2 , both forward and back titra-


Figure 1. Titration curve and its first derivative ($\text{dpH/d}[\text{OH}^-]$) of soil humic acid, KS-T1-HA: $[\text{HA}] = 0.2 \text{ g/l}$, $I = 0.1$ (NaClO_4), and $T = 25^\circ\text{C}$.

tions give almost identical results. A typical titration example is shown in Figure 1. The acid capacity is measured by the quantity of base needed to bring the solution to neutralization.¹² By taking the derivative of titration curve the end point can be accurately determined as shown also in Figure 1. The peak maximum appears around pH 7 which suggests that most of the functional groups are dissociated in the neutral pH range.

Molecular Size Distribution. The molecular size distribution for the soil humic acids are determined by ultrafiltration technique. The results are shown in Table 5 and further illustrated in Figure 2. As seen in this figure, the molecular size distribution patterns of two purified soil humic acids, KS-T1-HA and KS-T3-HA are similar, but they appear somewhat different for KS-T2-HA. The sodium salt of humic acid has higher contents of inorganic impurities, which affect the molecular volume of a polyelectrolyte. Figure 2 also

Table 5. Molecular Size Distribution Determined by Ultrafiltration at pH 8.5: Percentage Retention of Filter

Filter (nm)	Pore size (Dalton)	Aldrich-HA(Na^+) (%)	Aldrich-HA(H^+) (%)	KS-T1-HA(H^+) (%)	KS-T2-HA(Na^+) (%)	KS-T3-HA(H^+) (%)
15	3×10^5	7.3	5.0	12.3	11.4	10.1
5	1×10^5	25.0	10.3	13.7	8.5	15.6
3	5×10^4	46.0	31.0	31.1	—	37.0
2.1	3×10^4	59.7	54.7	58.3	33.9	45.8
1.5	1×10^4	76.7	73.7	76.5	66.0	72.9
1.3	5×10^3	83.0	85.3	86.9	81.5	81.8
1	1×10^3	94.3	94.7	95.6	95.0	93.6

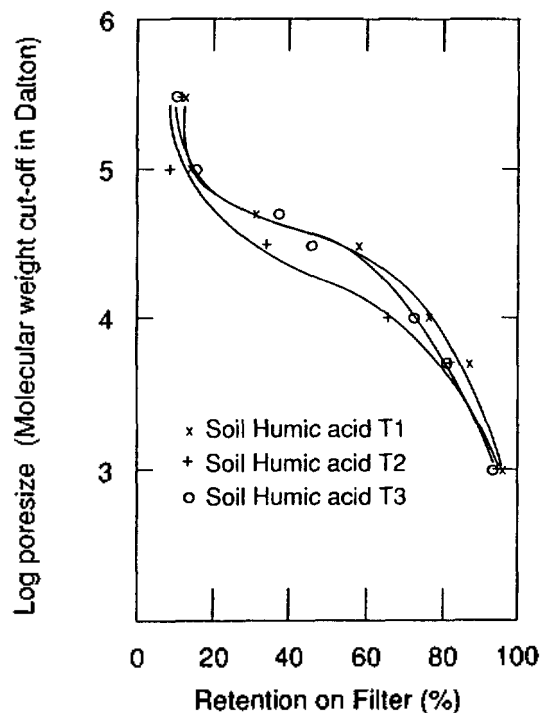


Figure 2. Molecular size fractionation of soil humic acids by ultrafiltration using different pore size filters: [HA]=30 mg/l, pH=8.5 and T=25°C.

shows that around 14-16% of soil humic acids has a molecular weight greater than 100,000 Daltons. In the lower mass range, about 20% has a molecular weight less than 5000 Daltons. The humic acids have mass which lie between these two values with an average of around 20,000 Daltons.

Conclusion

This initial work has demonstrated that humic acids can be extracted and purified for complexation studies in an aquatic solution with metal ions. The proton exchange capacity has been determined to quantify the functional groups of the humic acids available for complexation with metal ions.

Elemental analysis and ultrafiltration have produced results which provide a better insight into the nature of these soil humic acids. Spectroscopic study is in progress in order to elucidate some structural details of the soil humic acids.

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