



Compost humic acid-like matter as surfactant.

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Introduction

The capacity of a chemical compound to lower the water surface tension is a basilar property for most performances and applications. Surfactants for instances are useful for soil remediation and bioremediation (West and Harwell, 1992; Mulligan et al., 2001). In the presence of non aqueous phase liquid (NAPL), surfactants may cause dispersion of droplets and stabilization of the dispersion, thus improving the rate of removal by conventional methods. They are utilised within chemical-physical technologies like in situ soil flushing and ex situ soil washing for remediation of unsaturated zone and like pump and treat for aquifer remediation. In bioremediation, surfactants improve the bioavailability of organic compounds and consequently biodegradation rate. For example, some surfactants are able to remove one or two orders of magnitude more chlorinated organics than water alone by formation of microemulsions.

Humic acids are natural constituents of soil (Senesi and Loffredo, 2000) and waters (Boggs et al., 1985; Gasparovic and Cosovic, 2003) organic matter. Structural information allows to forecast for these compounds good properties as complexing agents, ion exchangers and surfactants. Most of their role in the natural environment is connected to these properties. Naturally occurring (Piccolo, 2002; Conte et al., 2001; Fava and Piccolo, 2002) and commercial (Koopal et al., 2004; Otto et al., 2003; Johnson and John, 1999) humic substances have been shown also suitable for soil bioremediation, biodegradable and non toxic for soil microbial biomass. These properties make humic-like substances highly desirable also as candidates for technological applications in many fields of chemistry, agriculture and soil science. Such perspective ap-

pears particularly intriguing nowadays in relation to the current issue of fossils versus renewable sources of chemical compounds (Chiellini and Solaro, 2003).

Humic acids may be obtained also from agro-industrial and municipal wastes by composting. Hereinafter we report experimental work on the surfactants properties of compost humic acids, as well as on their structure.

Core

The humic acid-like (HA) matter used in this work was isolated from mature compost obtained from municipal and lignocellulosic solid wastes in 1:1 v/v ratio. HA was available after extraction of the compost material with aqueous 0.1 M NaOH and 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$ (compost/liquid ratio 1:50 w/v) under N_2 , precipitation at $\text{pH} < 1.5$, extraction of the precipitated fraction with aqueous 2.82 MHF, washing with water to neutral pH and drying to obtain the final HA product in 12 % w/w yield.

HA exhibited very good surfactant properties in aqueous solution: i.e., critical micellar concentration (c.m.c.) = 403 mg/L, surface tension at c.m.c. (γ_{cmc}) = 36.1 mN/m and C_{20} (concentration of surfactant needed to lower the surface tension of 20 mN/m below the solvent surface tension) = 29.75 mg/L. These results appear quite remarkable when compared with values for other major commercial and research surfactants (Table 1). Particularly, the high cmc/C_{20} ratio of 13.5, compared to the values of about 2-4 for other commercial surfactants, evidences how the above compost HA is prone to adsorb rather than micellize.

According to elemental analysis, molecular weight measurements, NMR and IR spectroscopy data, the HA molecular structure is visualized as containing 26 oxyphenyl-propyl repeating units (r.u.), each one bonded to short and/or long hydro C chains to come up to an average of total 30 C atoms per r.u.. Several functional polar groups have been identified in this polymeric molecule, i.e., NH_2 , CONH , COOH , XOH , XOX , X = alkyl and/or phenyl. The whole structure appears well consistent with the good performance of the HA matter as surfactant. A mostly intriguing aspect is that such structure is available by natural processes and does not require any laboratory synthetic chemical reaction. This fact makes the above HA material very competitive for the low cost, in addition to the good properties. Since structures of humic-like substances vary greatly as a function of compost ingredients and composting time, composted wastes appear a very rich source of chemicals and/or ionic materials for application in many fields of chemistry, agriculture and soil science.

Conclusion.

It has been shown that compost humic acid-like matter (HA) has very good surfactant properties, which allow to propose use of this material in many fields. Compared to

other established commercial surfactants, HA has the advantage of very low cost. In fact, the material we have studied in this work has required only isolation from the compost mix and no further chemical modification. The results of this work stimulate also further work with compost organic matter. Indeed, chemical composition and structure of compost humic-like compounds varies greatly as a function of the compost ingredients and of the composting time. It is quite likely therefore that one could find in and isolate from compost products chemicals and/or ionic materials tailored for specific needs. Work for the use of compost HA in soil remediation is under way.

References

- Askvik, K.M., Gundersen, S.A., Sjoblom, J., Merta, J., Stenius, P., 1999. Colloid and Surfaces A: Physicochem. Eng. Aspects 159, 89.
- Boggs, J.R.S., Livermore, D.G., Seitz, M.G., 1985. J. Macromol. Sci. Rev. Macromol. Chem. Phys. C25(4), 599.
- Chiellini, E., Solaro, R., 2003. Biodegradable Polymers and Plastics. Kluwer Academic Plenum Publishers, New York.
- Conte, P., Zena, A., Pilidis, G., Piccolo, A., 2001. Environ. Poll. 112, 27.
- Dahanayake, M., Cohen, A.W., Rosen, M.J. 1986 J. Phys. Chem., 90, 2413.
- Fava, F., Piccolo, A., 2002. Biotechnology and Bioengineering 77, 204.
- Gasparovic, B., Cosovic, B., 2003. Estuarine, Coastal and Shelf Sci. 58, 555.
- Johnson, P.W., John, W.W., 1999. J. Contaminant Hydrology 35, 343.
- Koopal, L.K., Goloub, T.P., Davis T.A., 2004. J. Colloid and Interface Sci. 275, 360.
- Matsushita, Y., Yasuda, S. 2003. J. Wood Sci. 49, 166.
- Mulligan, C.N., Young, R.N., Gibbs, B. F., 2001. Engineering Geology 60, 371.
- Otto, H.W., Britten, D.J., Larive, C.K., 2003. J. Colloid and Interface Sci. 261, 508.
- Piccolo, A., 2002. Adv. Agron. 75, 57.
- Rana, D, Neale, G.H., Hornof, V., 2002. Colloid Polym. Sci. 280, 775.
- Rosen, M.J., 1989. Surfactants and Interfacial Phenomena, 2nd edition, Wiley, New York, p. 122.
- Senesi, N., Loffredo E., 2000. The chemistry of soil organic matter. In: Sparks, L., (Ed.), Soil Physical Chemistry. CRC Press,. New York, p. 239.

West, C.C., Hartwell, J.H., 1992. Environmental Sci. and Technol. 26, 2324.

Yanhua, J., Weihong, Q., Zongshi, L., Lubo, C., 2003. Tenside Surf. Det. 40, 77

Yanhua, J., Weihong, Q., Zongshi, L., Lubai, C., 2004. Energy Sources 26(4), 409.

Table 1. Performance parameters for various commercial and research surfactants

Surfactant	γ_{cmc}^a (mN/m)	c.m.c. ^b (% w/w)	c.m.c. ^b (M)	C
MP-SAL ^d (Matsushita and Yasuda, 2003)	45	0.30	-	
MKL ^e (Yanhua et al., 2003 and 2004)	38-28	0.26-0.41	-	
Borregaard Lignotech SL ^f (Askvik et al., 1999)	40	0.306	$4 \cdot 10^{-5}$	
Aldrich SL ^g (Rana et al., 2002)	67.8	10	$1.9 \cdot 10^{-3}$	
SDS ^h	39.5^i	0.231	$8.2 \cdot 10^{-3j}$	
CTAB ^k	36.5	0.033	$9 \cdot 10^{-4}$	
peat soil HA ^l	47.5	0.029-0.251	0.17-1.48	3
HA ⁿ	36.1	0.0403	$2.62 \cdot 10^{-5}$	2

0.1 ^a Surface tension at critical surfactant micellar concentration

^b Surfactant critical micellar concentration

^c Surfactant concentration needed to lower the solution surface tension by 20 mN/m below the solvent surface tension

^d Product of the Mannich reaction of phenolized sulfuric acid lignin.

^e Modified Kraft lignin

^f Sulfite liquor lignin: MW = (63-76) 10^3 , S % = 6.2

^g Sulfite liquor lignin: MW = 52000, S % = 5.2

^h Sodium dodecyl sulphate

ⁱ (Dahanayake, 1986)

^j (Rosen, 1989)

^k Cetyltrimethylammonium bromide; data obtained in this work.

^l (Terashima et al., 2004)

^m Data calculated by the authors of this work

ⁿ Humic acid-like matter isolated in this work