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NEW APPROACHES FOR ASSESSMENT AND IMPROVEMENT OF ENVIRONMENTAL STATUS IN BALKAN REGION: INTERACTIONS BETWEEN ORGANISMS AND ENVIRONMENT

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[P16]
Humic acid - ability to use as natural surfactants

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The structure characteristics of humic acids (HAs) indicate that they have amphiphilic properties, and can act as natural surfactants, ie. can reduce the surface tension of water forming at high concentrations similar to micelle structure.
HAs can be used as natural surfactants and can be proposed for technological applications. HAs extraction from the soil is very difficult and yields are very low. In contrast, biomass offers the possibility to obtain low cost HAs with good yields. This fact implicate the possibility of using biomass and municipal solid waste as a source of humic acids, which could replace synthetic surfactants in various applications. An interesting result in the use of surfactants as HAs has been given for the remediation of soil.
Remediation of soil means detoxification of polluting agents. In recent years the use of bioremediation wich uses microorganisms is rising for *in situ* degradation.
The ability of HAs to increase the solubility of contaminants was tested directly on the soil. Humic acids at a concentration of 10 mgL^{-1}, were able to remove a similar amount of pollutants and polycyclic aromatic hydrocarbons (PAH), thiophene, as same as SDS and Triton X-100.
HAs exhibit the properties of surfactants and can be used as substitutes for synthetic surfactants for various applications. However, to fully realize the idea of using humic acids as natural surfactants, it is necessary to establish adequate procedures for quality control, certification and labeling. Without this it would be difficult to promote as the substituents on the competitive market.
Our research results in connection with HAs, during *ex situ* bioremediation, also included in this paper.

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This research is a part of project III43004 funded by the Ministry of Education and Science of the Republic of Serbia.

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What are the surfactants?

Surface-active agents (surfactants) belong to a group of substances that at low concentrations are adsorbed onto the surface or interfaces of a system altering the free energy of those systems (Rosen, 2004). In the case of water as solvent, surfactant consists of a hydrophilic head and a hydrophobic tail. Inwater, surfactant molecules concentrate at the water–air interface, with the hydrophilic heads oriented towards the water and the hydrophobic tails oriented away from it (West and Harwell, 1992). When surfactants arrange themselves along the water–air interface, the surface tension of the solution decreases with increasing surfactant concentration until the surface tension is below a critical point. The concentration at which the critical point occurs indicates the formation of micelle structures and it is defined as the critical micelle concentration (CMC) (Haigh, 1996). A hydrophobic molecule in contact with an aqueous solution containing surfactant tends to arrange itself within the core of the micelles. Therefore the hydrophobic core of the micelle structure enables the surfactant to enhance the aqueous solubility of hydrophobic organic compounds, increasing their apparent solubility (West and Harwell, 1992)

Humic acids molecules as natural surfactants

Humic acids (HAs), one of the most important fraction of humic substances are composed of hydrocarbon chains that come from a relatively unchanging segments of plant polymers, and hydrophilic fraction, which mainly consist of ionic groups such as carboxylic acids, and the non polar compounds such as phenols, alcohols, aldehydes, ketones, amides and amines. These characteristics indicate that humic acids have amphiphilic properties, and can act as natural surfactants, ie. can reduce the surface tension of water forming at high concentrations similar to micelle structure.

Chemical characterization of humic acids

Surface tension and CMC values for HA-surfactants extracted from different raw materials [Quadri et al. (2008), Savarino et al. (2010), Adani et al. (2010)]

Type of HA's	Atomski odnos			^{13}C NMR				HB/HI	CMC* (mg L^{-1})	Surface tension (mN m-1)
	C/N	C/H	O/C	% Alkyl-C 0-45 ppm	% O/N Alkyl-C 45-110 ppm	% Aromatic-C 110-160 ppm	% Carbonyl-C 160-220 ppm			
From biomass	13,9	0,75	0,4	40	30,7	18,1	10,9	1,4	712	43,5
From municipal and green waste	13,7	0,8	0,3	46,5	28,4	14,7	10,6	1,61	750	38
From plants	18	0,7	0,4	24	45	22	9	0,86	1986	43

* CMC value experimentally determined

Legend:
CMC – Critical mycelar concentration
HB/HI – ration between hydrophobic vs. hydrophilic C, in which, HI = percentage of hydrophilic carbon calculated as the sum of the 13C CP MAS NMR area of [(45–110)+(160–220) p.p.m.] and Hb = percentage of hydrophobic carbon calculated as the sum of the 13C CP MAS NMR area of [(0–45)+(110–160)] p.p.m.

Humic acids as natural surfactants: technological applications

Remediation of soil consisting of detoxification of polluting agents. In recent years the use of bioremediation is rising, which uses microorganisms to *in situ* degradation, but this technique has some limitations in terms of appropriate soil conditions for their activity. To be rehabilitated contamination of persistent organic pollutants, recent attention has focused on the possibility of desorption of contaminants from contaminated soil *in situ* technologies (irrigation area) or *ex situ* (soil washing). These technologies are based on the principle of separation of adsorbed pollutants from land to water with added surfactants.

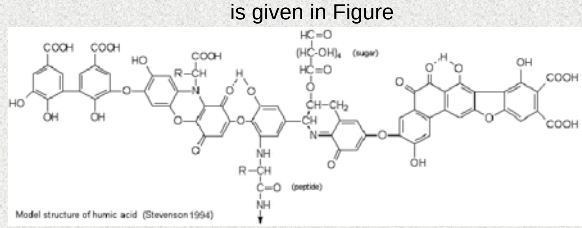
The ability of HAs to increase the solubility of contaminants was tested directly on the soil. Humic acids at a concentration of 10 mgL-1, were able to remove a similar amount of pollutants and polycyclic aromatic hydrocarbons (PAH), thiophene, as same as SDS and Triton X-100.

HAs exhibit the properties of surfactants and can be used as substitutes for synthetic surfactants for various applications. However, to fully realize the idea of using humic acids as natural surfactants, it is necessary to establish adequate procedures for quality control, certification and labeling. Without this it would be difficult to promote as the substituents on the competitive market.

Our research results in connection with HAs, during *ex situ* bioremediation, also included in this paper.

The ability of HAs to arrange themselves so as to have their internal hydrophobic groups (hydrocarbon) and hydrophilic portions outwards, such as carboxyl, phenols and hydroxyl groups, depends on the length and flexibility of their constituent chains. Intramolecular aggregation of HAs plays an important role in the micelle formation, and long flexible HA polymers are considerably the best sequestrating agents (Engebretson and Von Wandruszka, 1997). The presence of nitrogen compounds in HAs seems, also, to affect CMC (Quadri et al., 2008), in agreement with what was reported for the synthetic surfactant. Amides have been reported to be incorporated in the aggregate/micelle lowering CMC. Amide molecules are probably adsorbed at the outer portion of the micelle, close to the water–micelle interface reducing the work required for micellization, as a consequence of the reduction of the mutual repulsion of the polar groups (COO–) of HA (Rosen, 2004).

Hypothetical structure of humic acids by Stevenson is given in Figure



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