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Green chemistry approach in treatment of waste water emulsions from metal-processing industries

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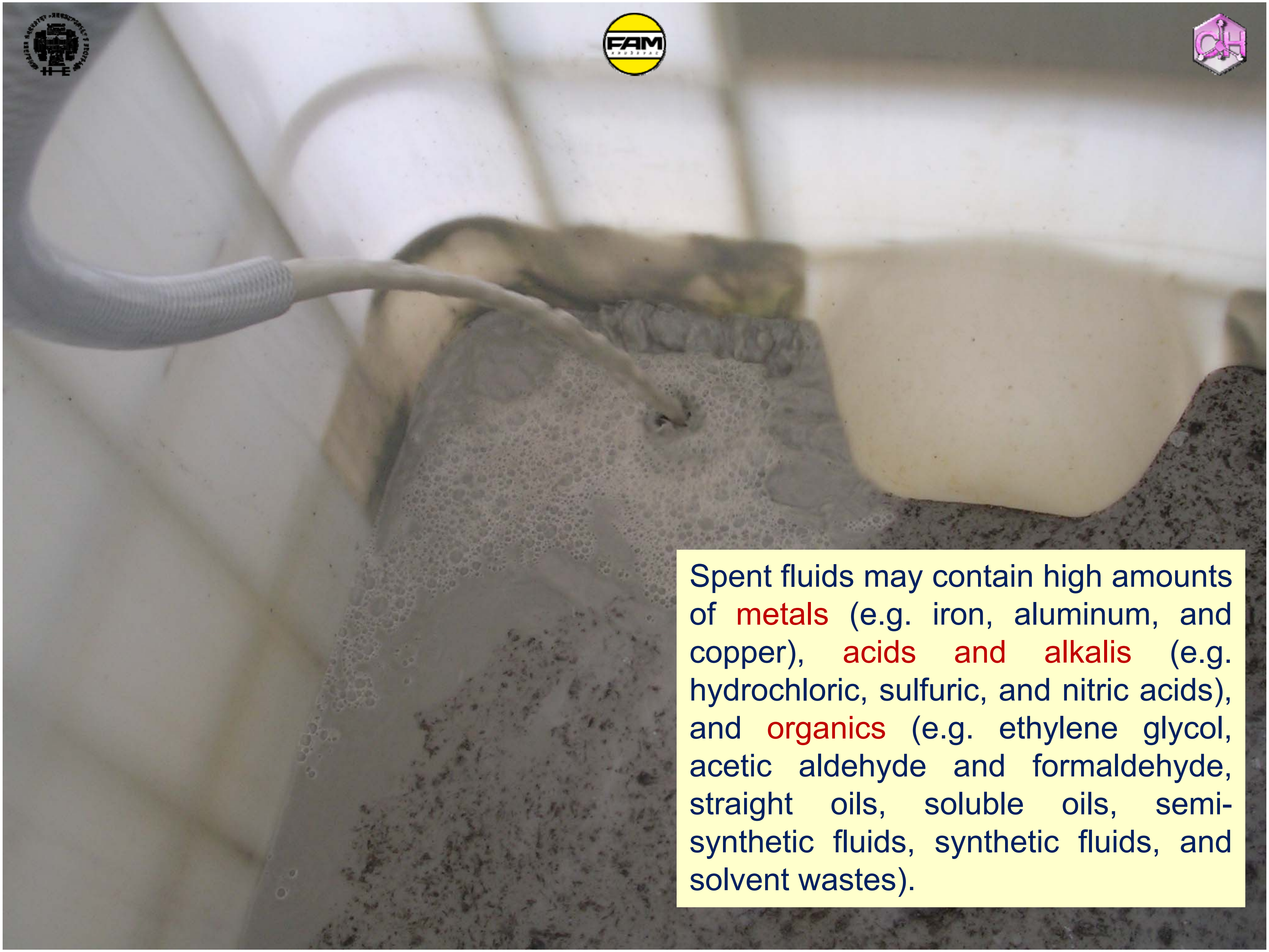
Metal working industries generate different kinds of wastewaters as a result of processing metal parts/products, and machinery, as well as result of associated activities such as manufacturing, and rebuilding/maintenance.

Oils used in metal working industries consist from mineral base and appropriate pack of additives. Oils for this purpose are used as an emulsion in water with detergents, biocides, chlorinated paraffin, halogenated and non halogenated additives, and additives included to improve performance.

Emulsions are used to cool and lubricate the machining tools and remove chips and swarfs from the cutting zone. After needed properties were lost or declared time limits were reached, used metal working emulsions have to be exchanged with new one.

Emulsion: typically 2-5% oil in water.



Spent fluids may contain high amounts of metals (e.g. iron, aluminum, and copper), acids and alkalis (e.g. hydrochloric, sulfuric, and nitric acids), and organics (e.g. ethylene glycol, acetic aldehyde and formaldehyde, straight oils, soluble oils, semi-synthetic fluids, synthetic fluids, and solvent wastes).

METHODS OF WASTE WATER/OIL MIXTURES TREATMENT:

- Gravity separators
- Skimmers
- Centrifuge
- Hydro cyclones
- Evaporators
- Filters
- Flocculation/coagulation
- Ultra-filtration
- Incineration

The 12 Principles of Green Chemistry (1-6)

(Anastas and Warner, 1998)

1. Prevention

It is better to prevent waste than to treat or clean up waste after it has been created.

2. Atom Economy

Synthetic methods should be designed to maximise the incorporation of all materials used in the process into the final product.

3. Less Hazardous Chemical Synthesis

Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to people or the environment.

4. Designing Safer Chemicals

Chemical products should be designed to effect their desired function while minimising their toxicity.

5. Safer Solvents and Auxiliaries

The use of auxiliary substances (e.g., solvents or separation agents) should be made unnecessary whenever possible and innocuous when used.

6. Design for Energy Efficiency

Energy requirements of chemical processes should be recognised for their environmental and economic impacts and should be minimised. If possible, synthetic methods should be conducted at ambient temperature and pressure.

The 12 Principles of Green Chemistry (7-12)

(Anastas and Warner, 1998)

7. Use of Renewable Feedstocks

A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

8. Reduce Derivatives

Unnecessary derivatization (use of blocking groups, protection/de-protection, and temporary modification of physical/chemical processes) should be minimised or avoided if possible, because such steps require additional reagents and can generate waste.

9. Catalysis

Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

10. Design for Degradation

Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.

11. Real-time Analysis for Pollution Prevention

Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

12. Inherently Safer Chemistry for Accident Prevention

Substances and the form of a substance used in a chemical process should be chosen to minimise the potential for chemical accidents, including releases, explosions, and fires.

Industrial (white) biotechnology: The application of indigenous and/or scientific knowledge to the management of (parts of) microorganisms, or of cells and tissues of higher organisms, so that these supply goods and services of use to the food industry and its consumers.

Green Chemistry: The utilisation of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products.

Bioremediation: Any process that uses biological systems, microorganisms, fungi, green plants or their enzymes to return the natural environment altered by contaminants to its original condition. It is based on the extremely diverse metabolic potential of natural microbial communities.

Bioremediation is a place where White biotechnology meets Green chemistry and its principles.

Metal-processing industries produce a large volume of oil-in-water emulsions together with other small organic molecules present as additives. After being used the fluids become less effective because of thermal degradation and contamination and must be replaced.

Our approach: flocculation, coagulation, precipitation, filtration, adsorption and bioremediation.

Emulsion contained 1–5% of oil.

Goal was to separate 95-99% of water and to discharge it in accordance with local regulations.

Scale up: from laboratory samples and probes (**1-10 L**) via pilot level (**2 m^3**) and finally up to the industrial level (**600 m^3** in total)

Stage I
Water separating

Phase I
Emulsion breaking-**flocculation**, **coagulation, precipitation**
(inorganic salts, base, amphoteric polyelectrolyte and precipitator)

Phase II
Two-step filtration:
Sand **filtration** / **adsorption-filtrations** (polyfunctional fillers)

Stage II
Microbiological treatment of yielded oil (**bioremediation**)

PRINCIPAL SCHEME AND SCALE UP

Principal scheme

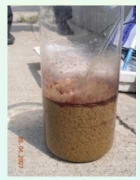
Homogenization
↓
pH adjustment
↓
Flocculation
↓
Coagulation
↓
Precipitation
↓
Sand filtration
↓
Adsorption/filtrations

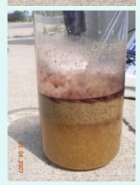
Water → Sanitary sewer

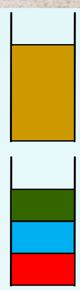
Sludge → Bioreme-diation

Laboratory scale

NaOH/HCl





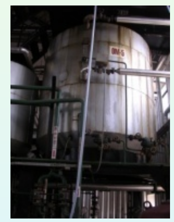


pH
COD
BOD
T°C
κ
Color
NTU

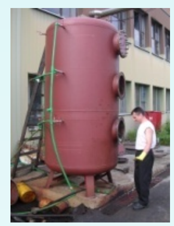
Biodegradation test

Industrial scale

$2x300\ m^3$
Homogeni-zation



$10\ m^3$
pH adjustment
Flocculation
Coagulation



$4\ m^3$
Sand filtration

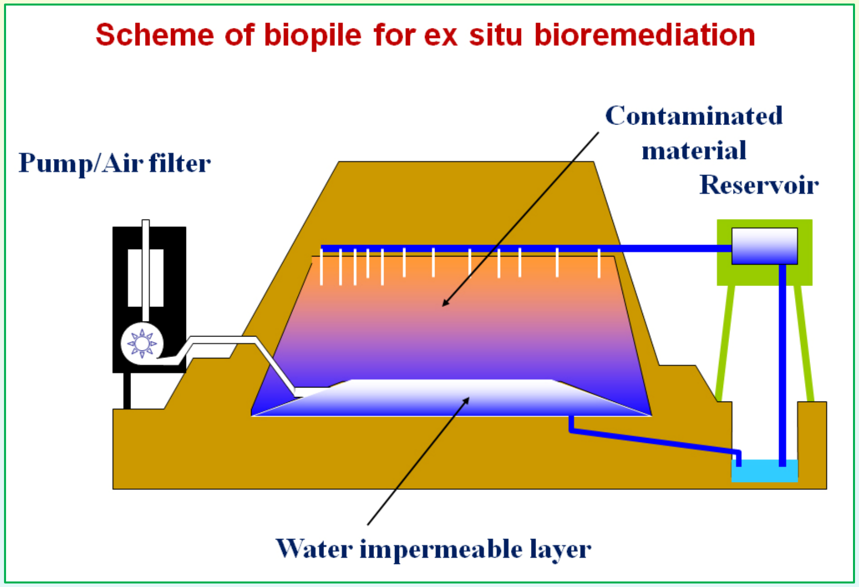
$2x2\ m^3$
Adsorption/filtration

$500\ m^3$
Bioreme-diation

COD [mg/O_2L]

100000
↓
5-10000
↓
100

EX SITU BIOREMEDIATION ON 500 m^3 BIOPILE



GAS CHROMATOGRAMS OF TPH EXTRACTS

Fig 1. Start of the bioremediation

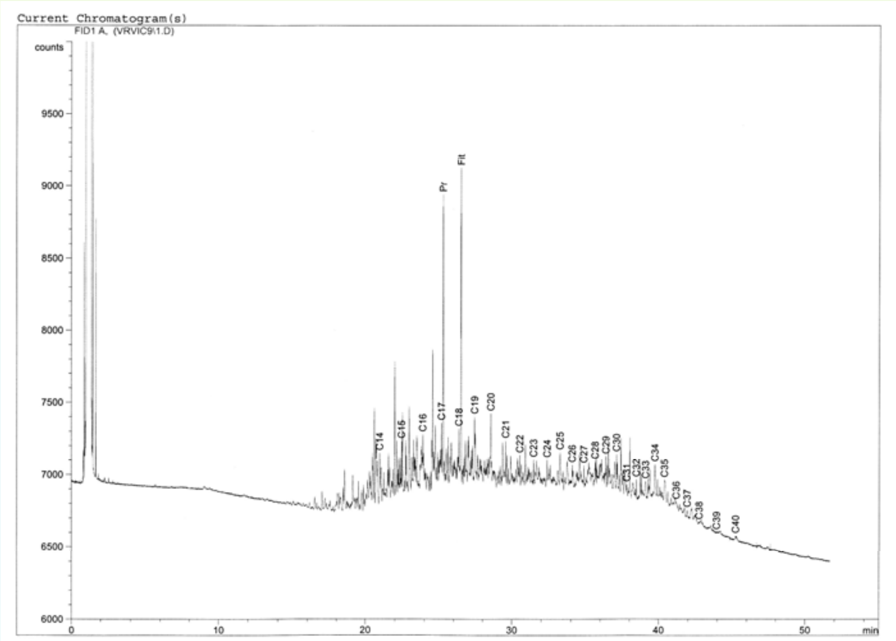
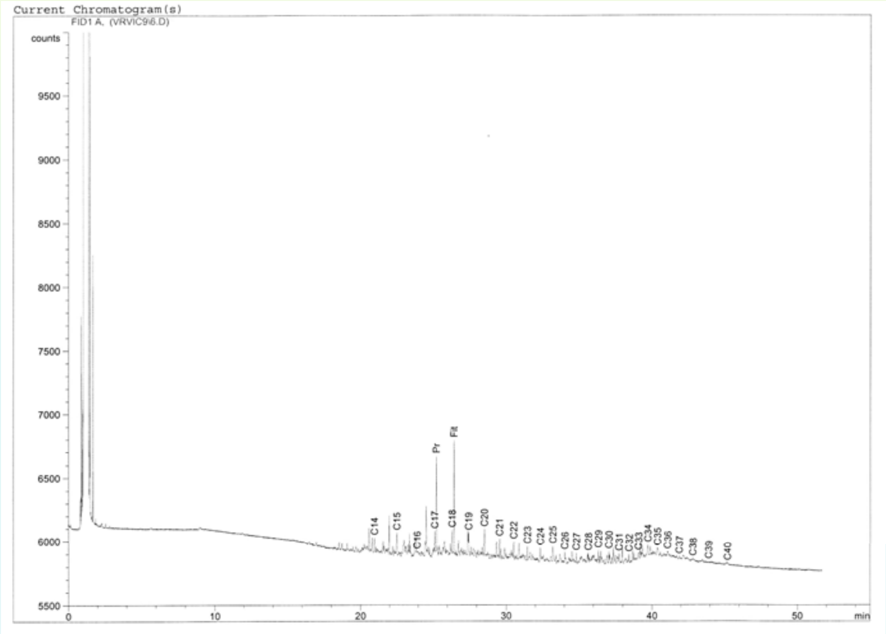
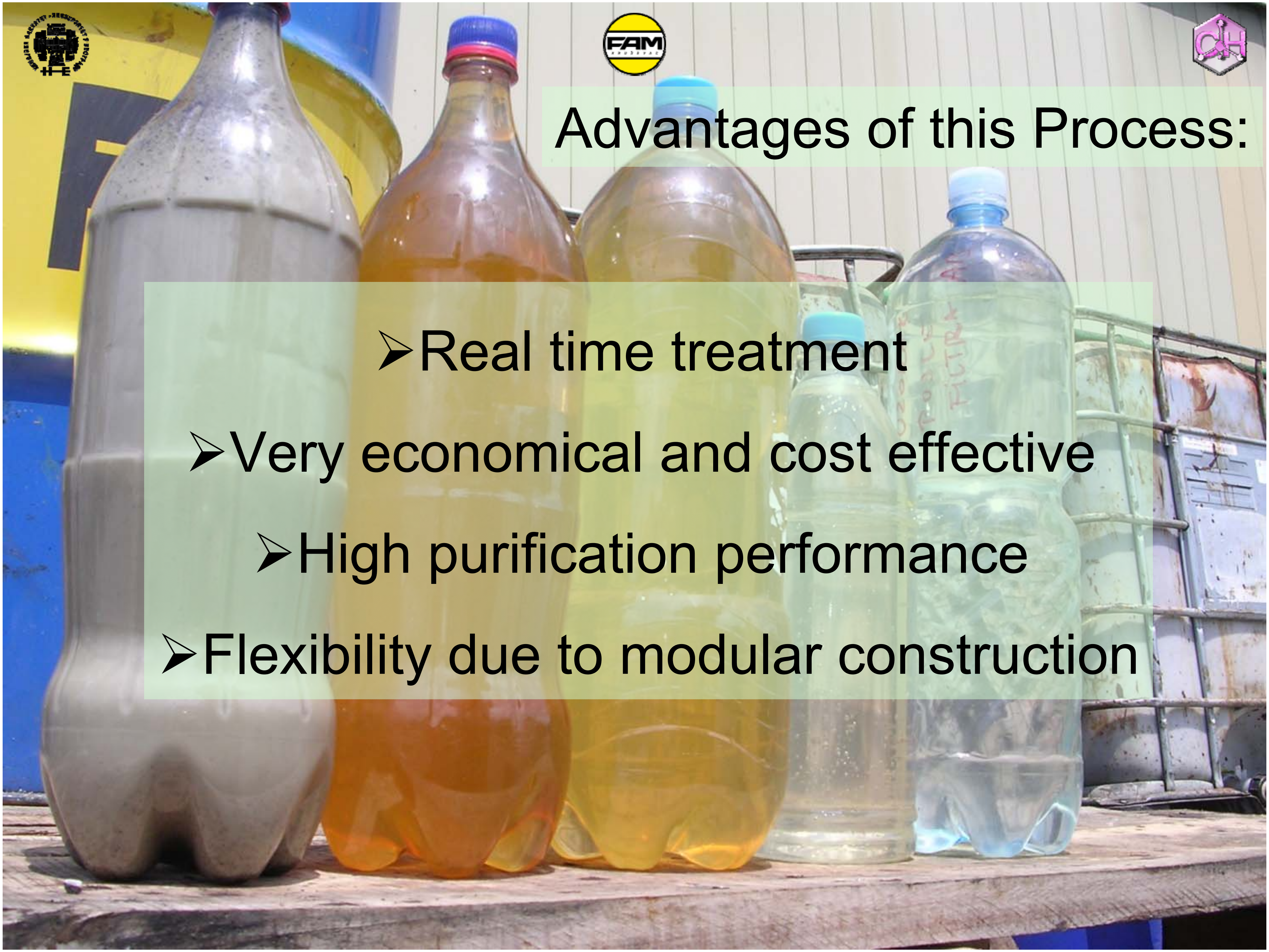


Fig 2. GC of TPH after 90 days



pH	H_2O [%]	$CaCO_3$ %	Humus %	TPH [g/kg]	N %	S %	C %	TOC	P_2O_5 [mg/100g]	K_2O [mg/100g]
7.64	21.88	5.00	4.94	0.48	0.074	0.146	3.728	2.865	32.60	38.20

Metal	Cu [mg/kg]	Zn [mg/kg]	Mn[mg/kg]	Co [mg/kg]	Pb [mg/kg]	Cd [mg/kg]	Ni [mg/kg]	Cr [mg/kg]	As [mg/kg]
	13.10	48.54	236.00	5.99	14.77	0.09	49.80	23.03	4.62
MPC	100.00	300.00	/	10.0	100.00	3.00	50.00	100.00	25.00



Advantages of this Process:

- Real time treatment
- Very economical and cost effective
- High purification performance
- Flexibility due to modular construction

GREEN CHEMISTRY IS ABOUT:

Reducing

- **Waste**
- **Materials**
- **Hazard**
- **Risk**
- **Energy**
- **Cost**

Microorganisms and enzymes derived from them can be used as biocatalysts to chemically modify organic molecules in industrial processes. Biocatalysts offers several advantages: substrate specificity, enantioselectivity, regioselectivity, mild process conditions, environmentally friendly processes. This is why we speak of “green chemistry”.

Is our future "green"?


Thank you for your attention