Water and Soils Clean-up from Mixed Contaminants

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Aim

- **for the remediation of contaminated land from representative heavy metals (e.g. Pb, As, Cr, Cd, Hg), POPs (lindane,atrazine, obsolete pesticides) and synthetic dyes (reactive blue, red, black from textile industry)**
- **developing novel Fe/Cu/carbon clean-up devices, as well as utilising SRB, SOB, FeSOB and advanced oxidation techniques for treatment of contaminated land and waters**

WATER – the Issue

Fresh water … NOT an infinite source

Population … 7.2 billion… growing

- substance essential for life
- strategic resource for every country/population
- elementary for everyday life (in developed

Pollution – the

Adsorbents

Natural/ commercial materials

zeolites, activated carbons, clays etc.

– known as good adsorbents of cations (Cd, Cu, Pb, Zn…),

– good adsorbents of organic pollutants (chlorinated organic solvents, organochlorine pesticides, and polychlorinated biphenyls)

– limited or no affinity towards toxic anions.

Composite adsorbents

Iron, Copper oxides/oxyhydroxides

– good adsorbents of anions/oxyanions (**As, Cr**, Se, Mo...)

– nanomaterials ... difficult use in practical application,

- legislation restricting the use of free engineered nanoparticles - applied in EU in the near future

- the total global investment in nanotechnologies was around 10 billion US dollars in 2005 (Navaro et al., 2008),

- it is estimated that the annual turnover of all ENPs based nanotechnologies will be in the range of 1.1-2.5 trillion US dollars by 2015 (Lux Research, 2006

Target

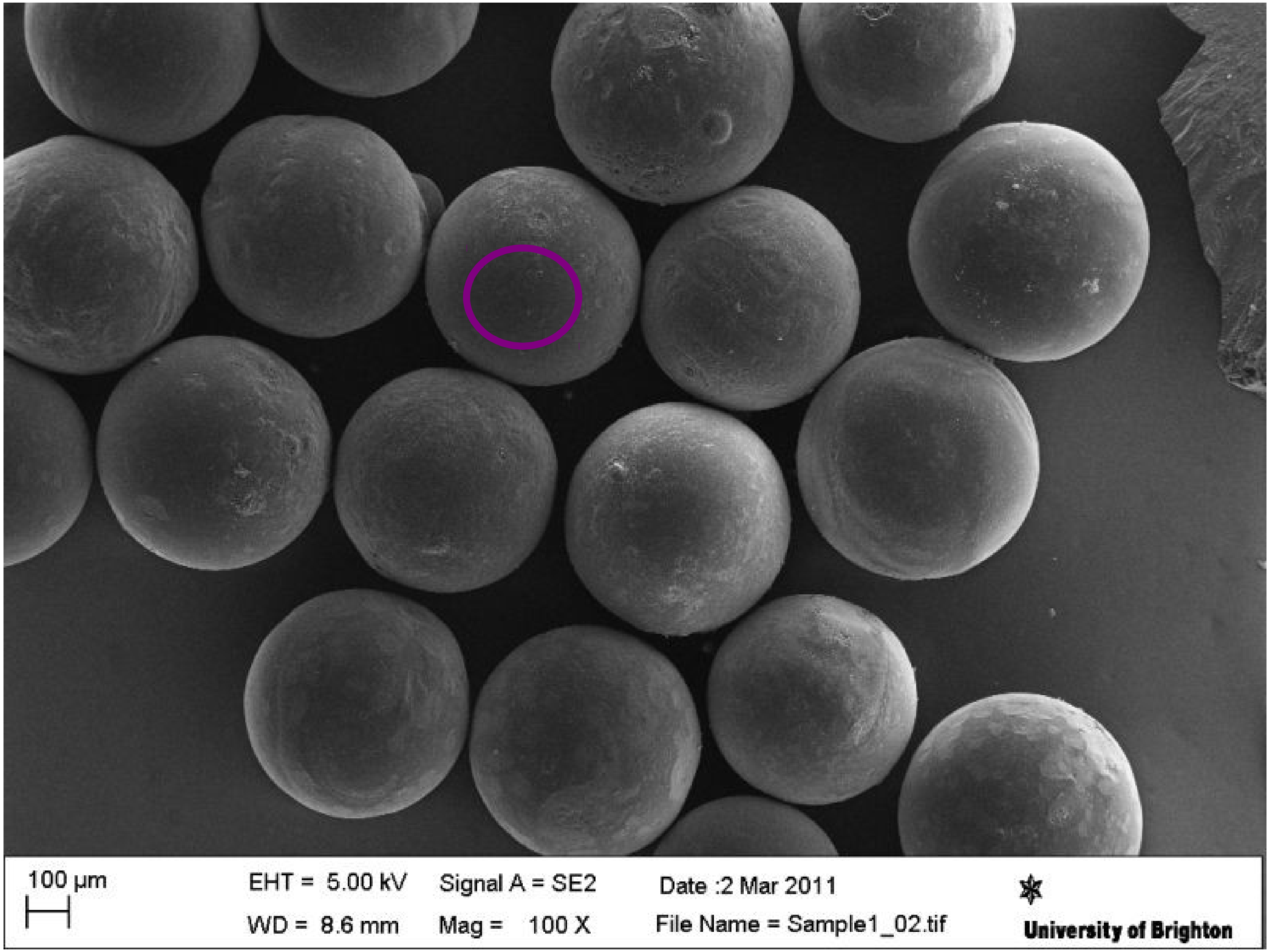
To prevent uncontrolled release of free ENPs to the environment (knowing the fate and migration routes through the soil zones)

To threat MIXED CONTAMINATS (organic and inorganic) in soils and waters

To develop composite sorbent materials, which will be suitable for removal of anions, while retaining affinity towards cations and organics

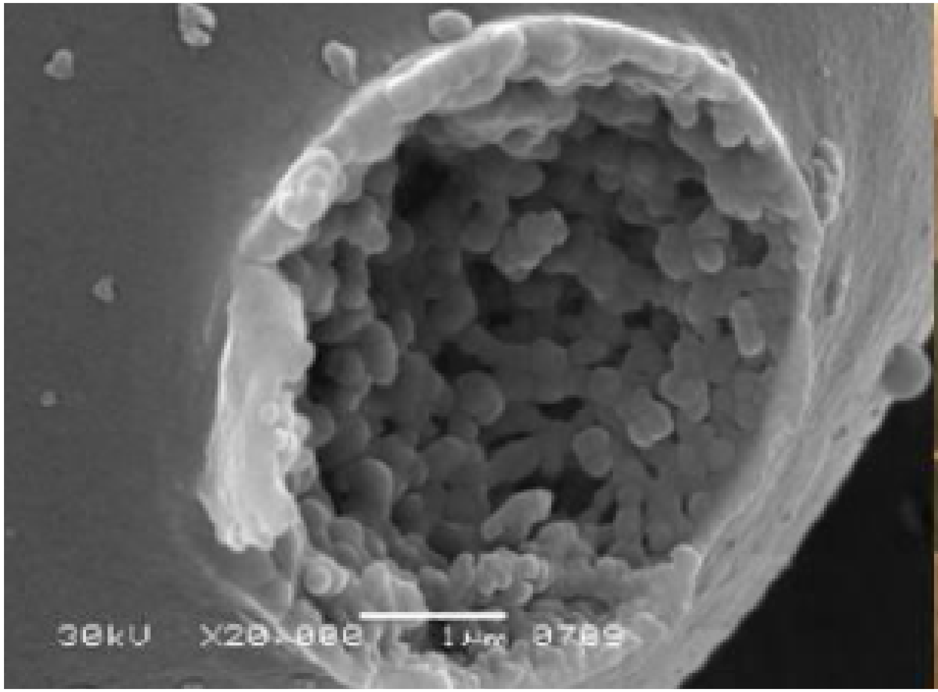
Carbon- MAST Carbon Int. Ltd

Carbon particles: 500-600 μm



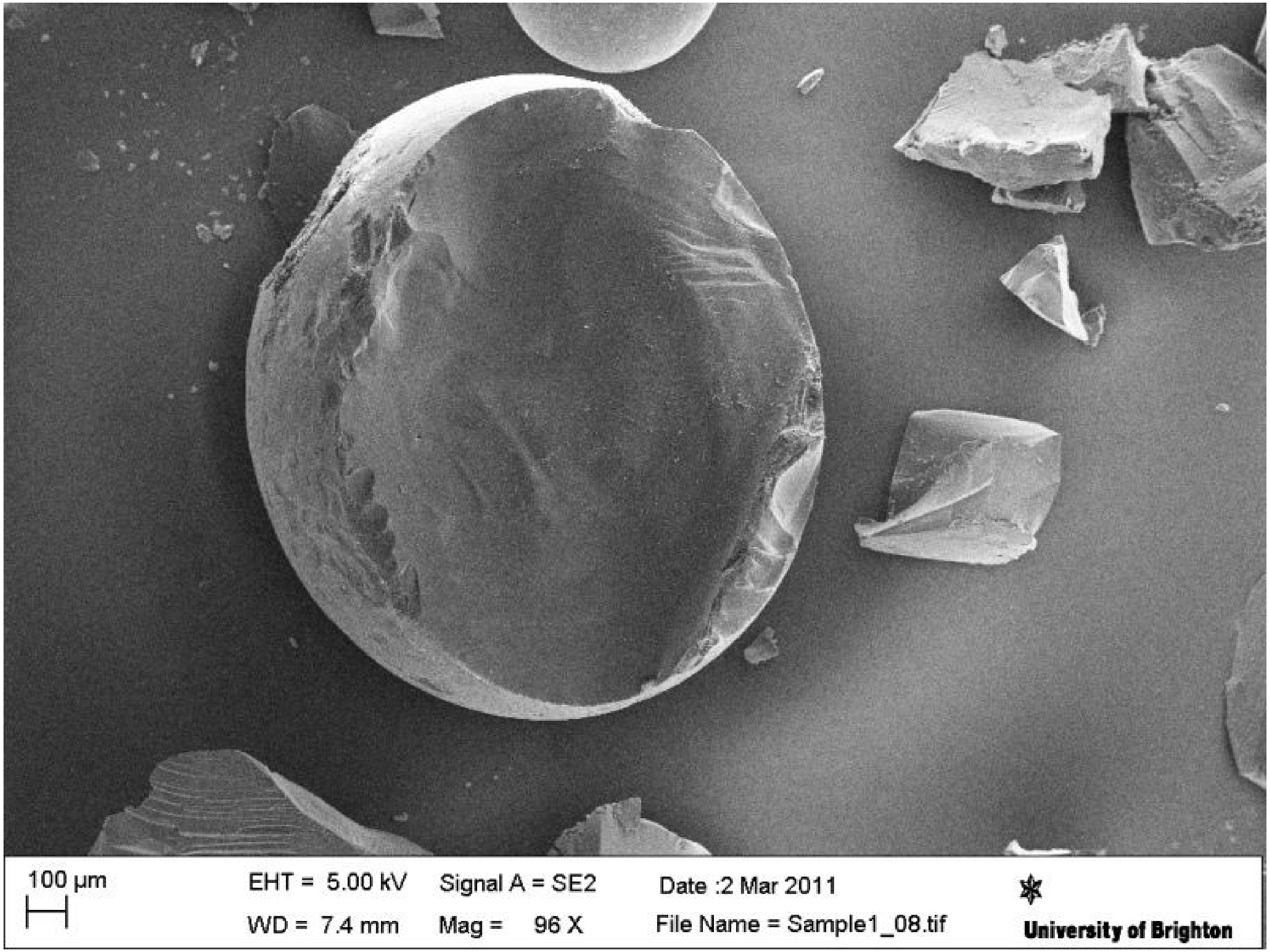
Carbon – MAST Carbon Int. Ltd

Carbon particles: 500-600 μm



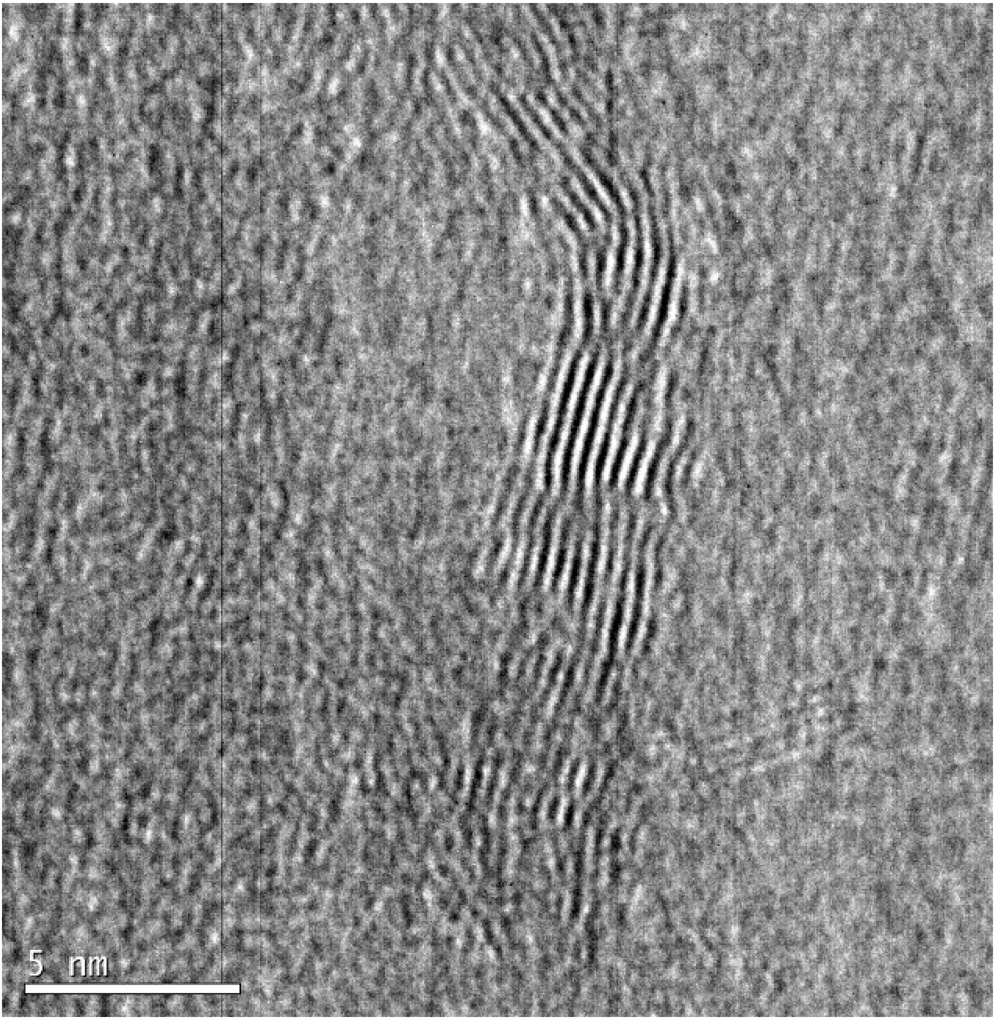
Carbon – MAST Carbon Int. Ltd

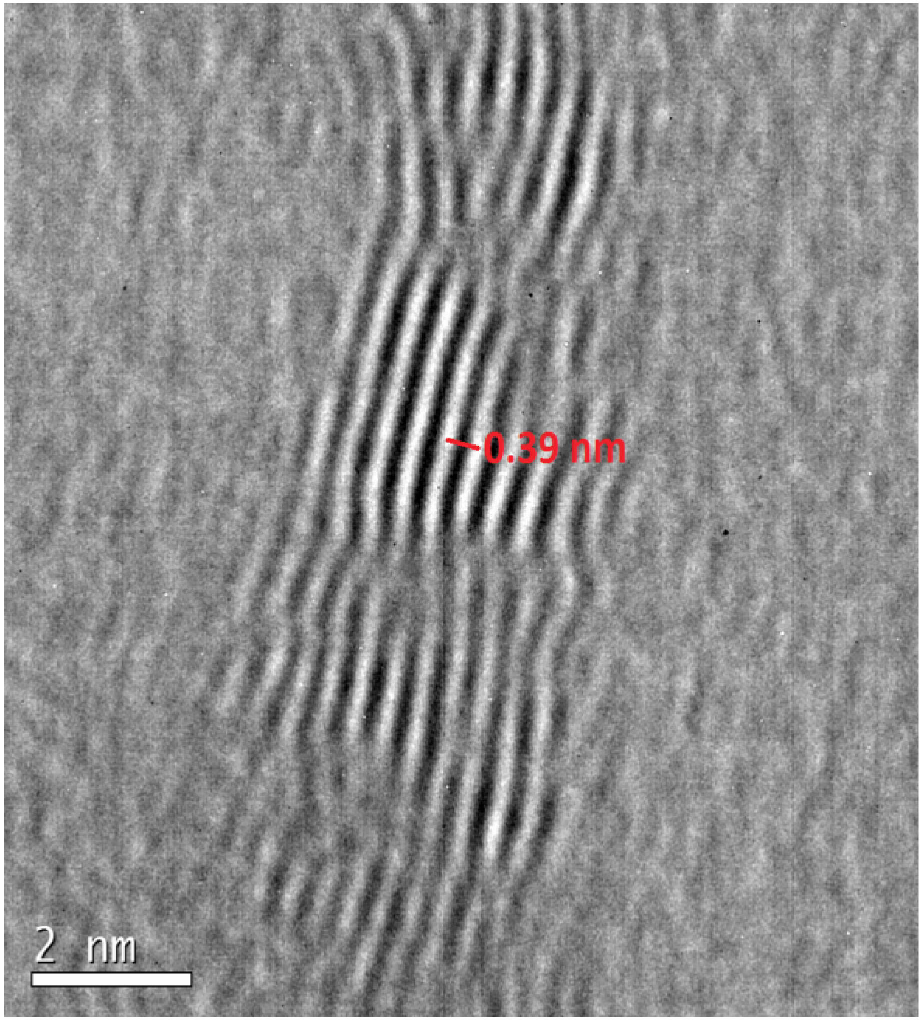
Carbon particles: 500-600 μm



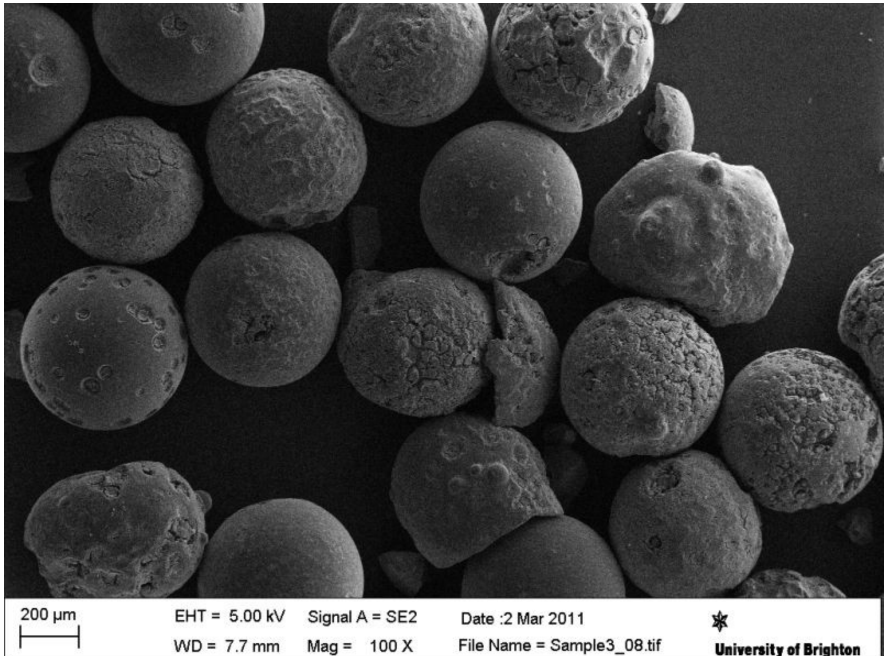
Carbon – MAST Carbon Int. Ltd

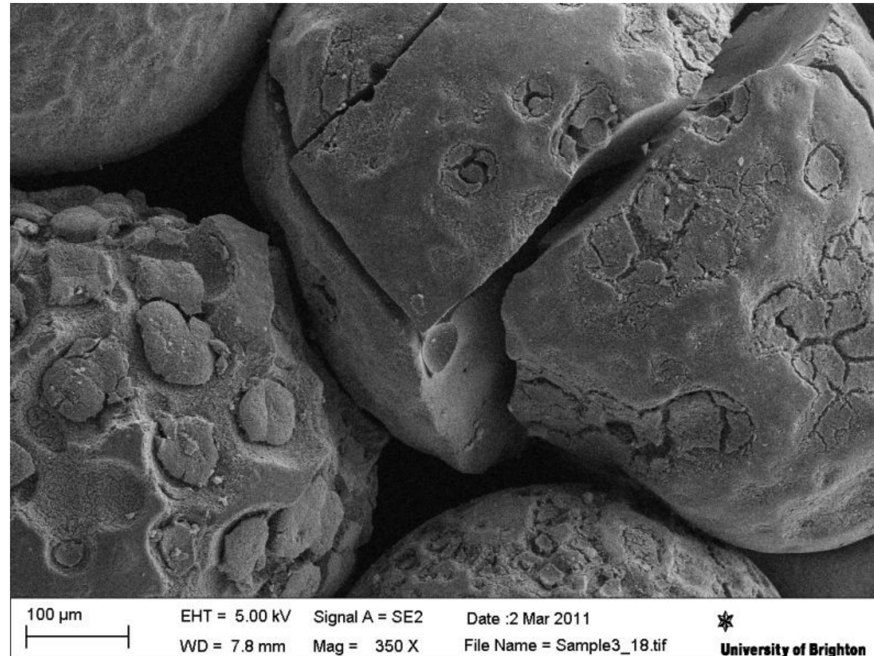
Carbon particles: HR-TEM

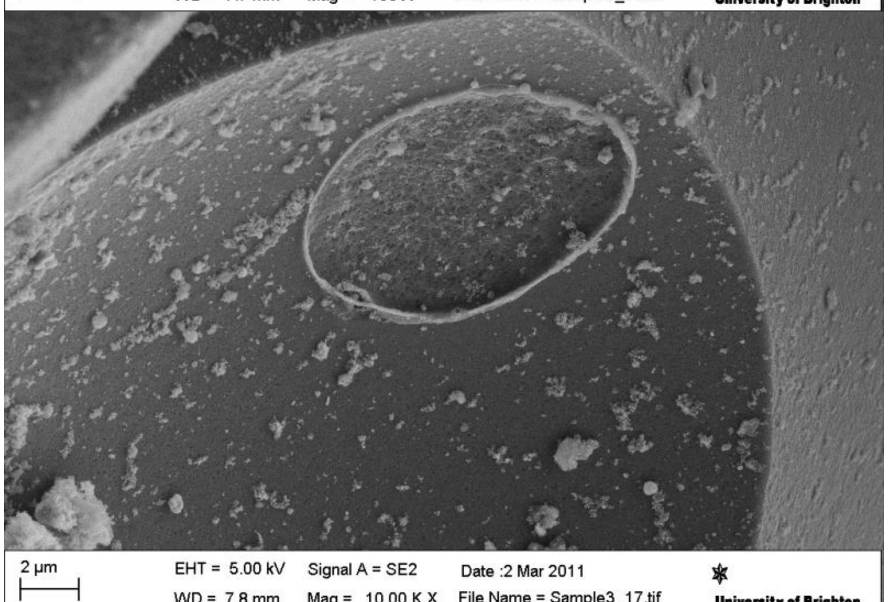


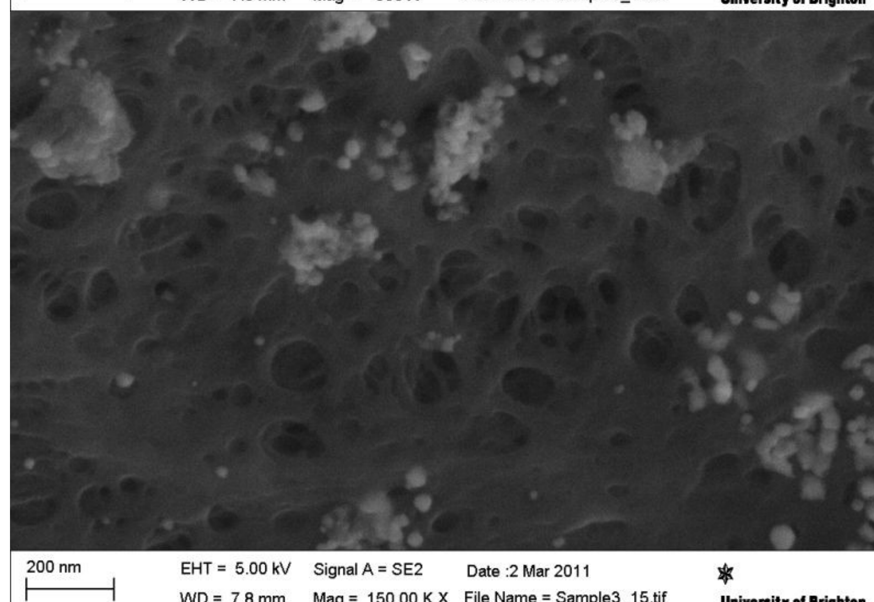


Fe-carbon: 500-600 μm

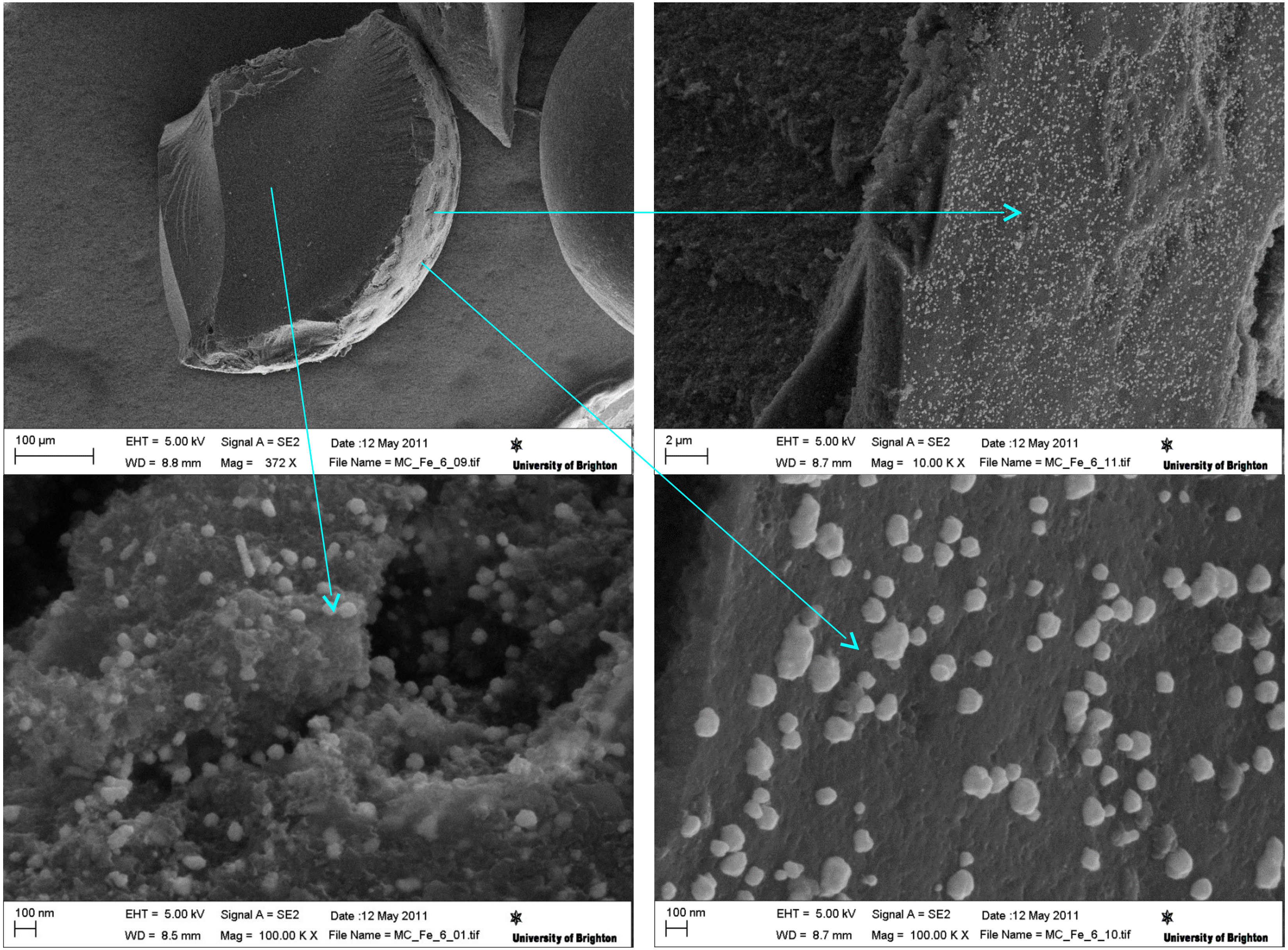




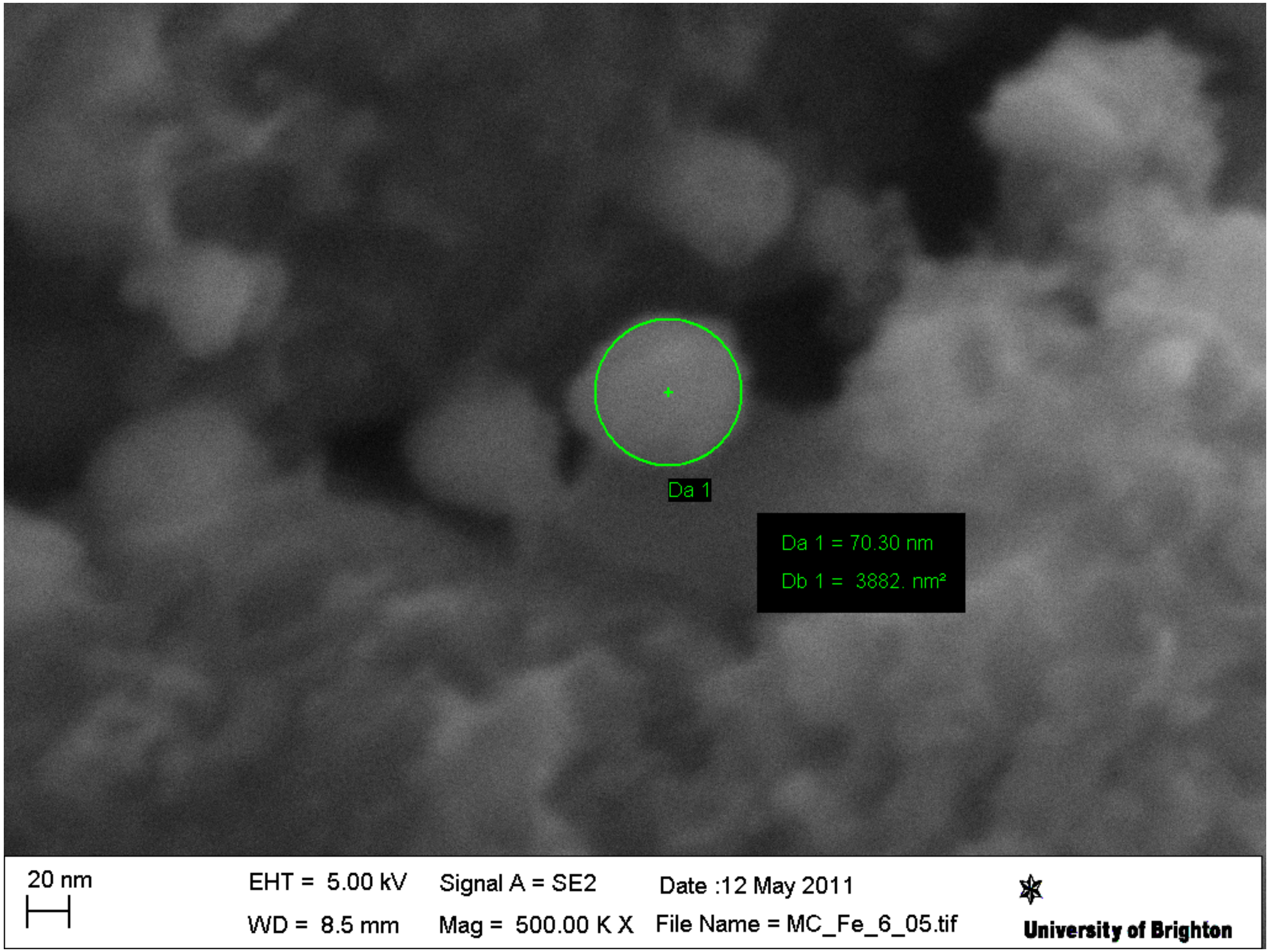




Fe-Cu-carbon: 500-600 μm



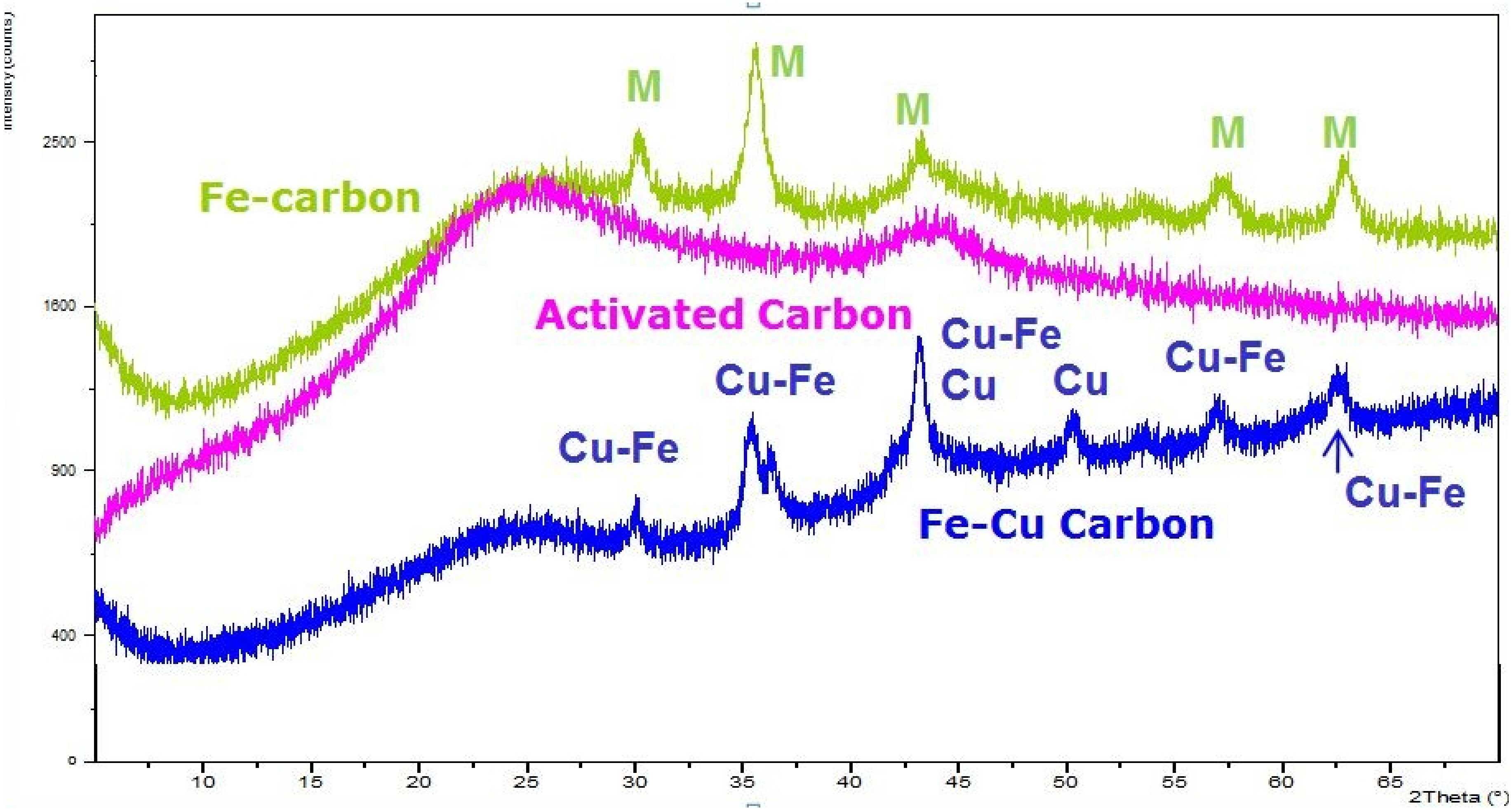
Fe-Cu-carbon



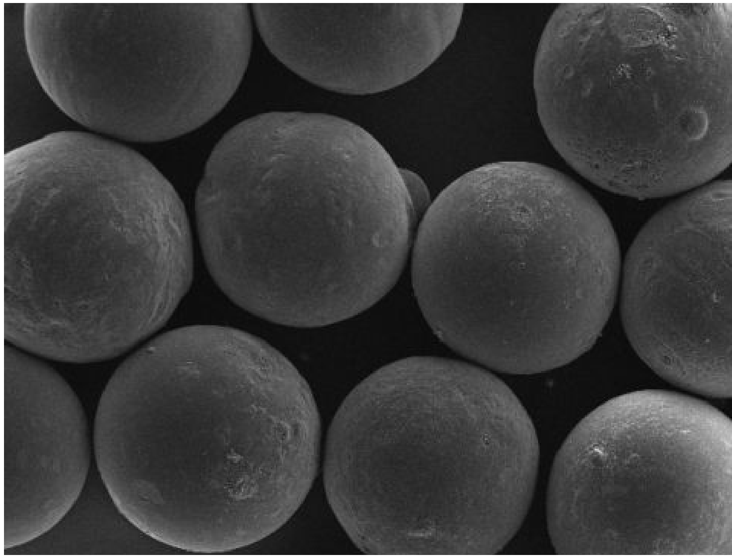
Da 1
Da 1 = 70.30 nm
Db 1 = 3882. nm²
20 nm
EHT = 5.00 kV
WD = 8.5 mm
Signal A = SE2
Mag = 500.00 K X
Date :12 May 2011
File Name = MC_Fe_6_05.tif
University of Brighton

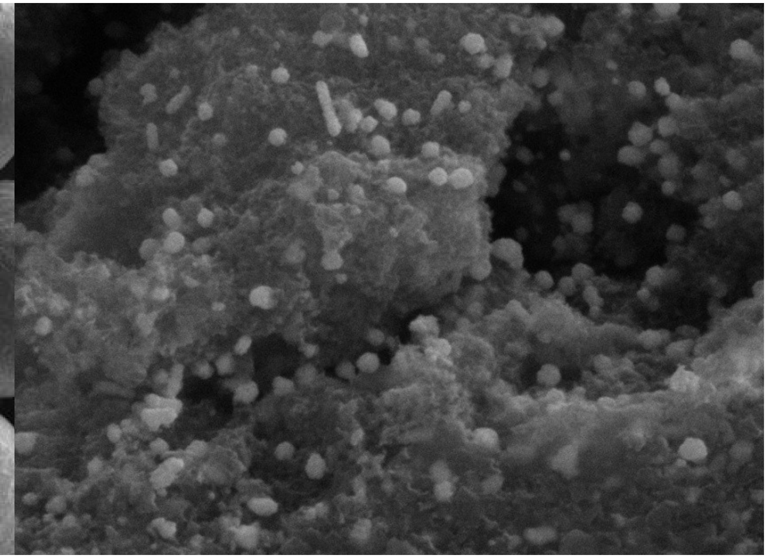
Material study

Fe-Carbon; Fe-Cu-Carbon

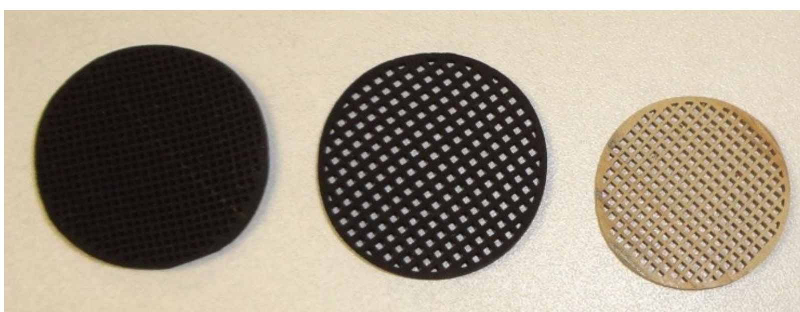


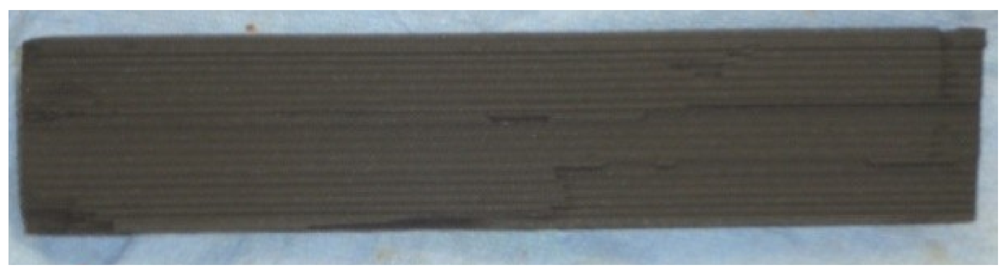
Monolyths





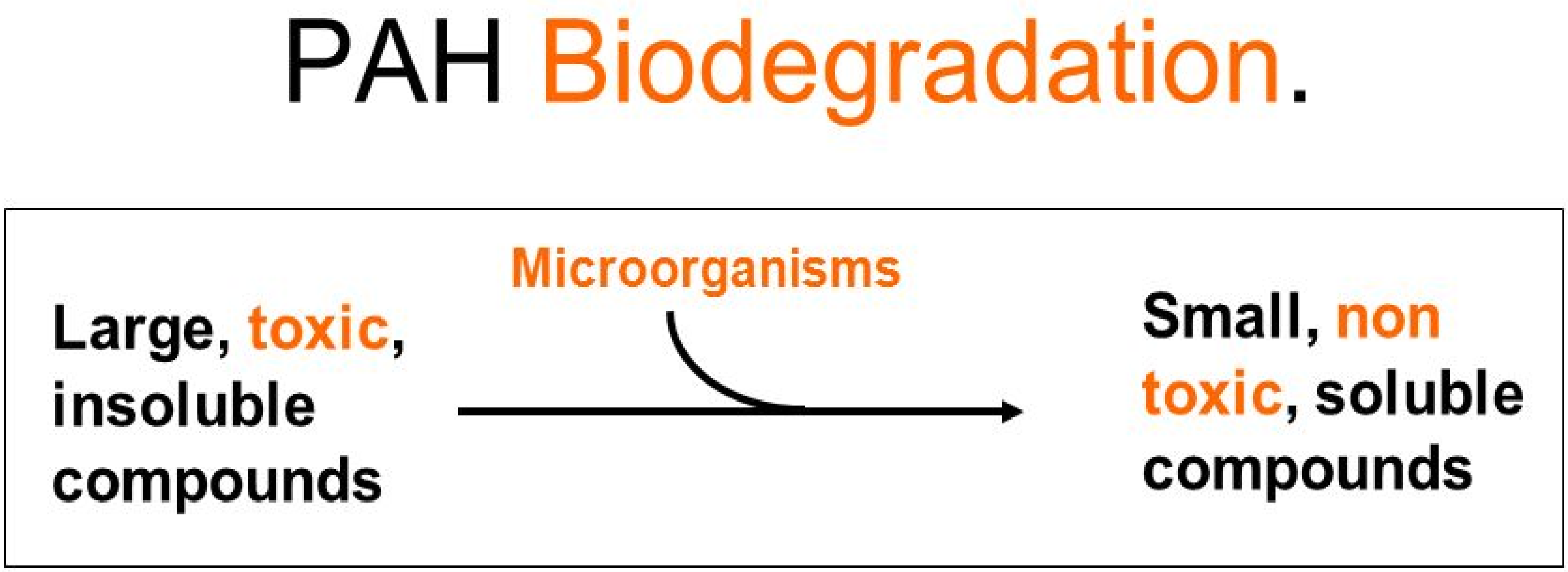
Embedding of NP to Monolyths





Bioremediation - POPs

The ultimate goal of any degradation process is complete mineralization of the organic contaminants, resulting in carbon dioxide, water



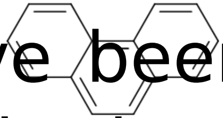
https://slideplayer.com/slide/10679009/

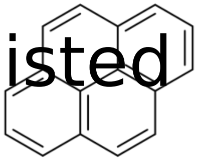
Polycyclic aromatic hydrocarbons (PAHs)

- Polycyclic aromatic hydrocarbons are compounds with two or more fused aromatic rings.

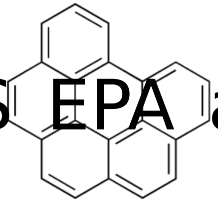
- They are hardly soluble in water and have high affinity for sorption on the surface of solid materials. So they are highly recalcitrant and persistent molecules in the environment.

- 16 PAHs have been listed by the US EPA as priority pollutants.


phenanthrene


pyrene

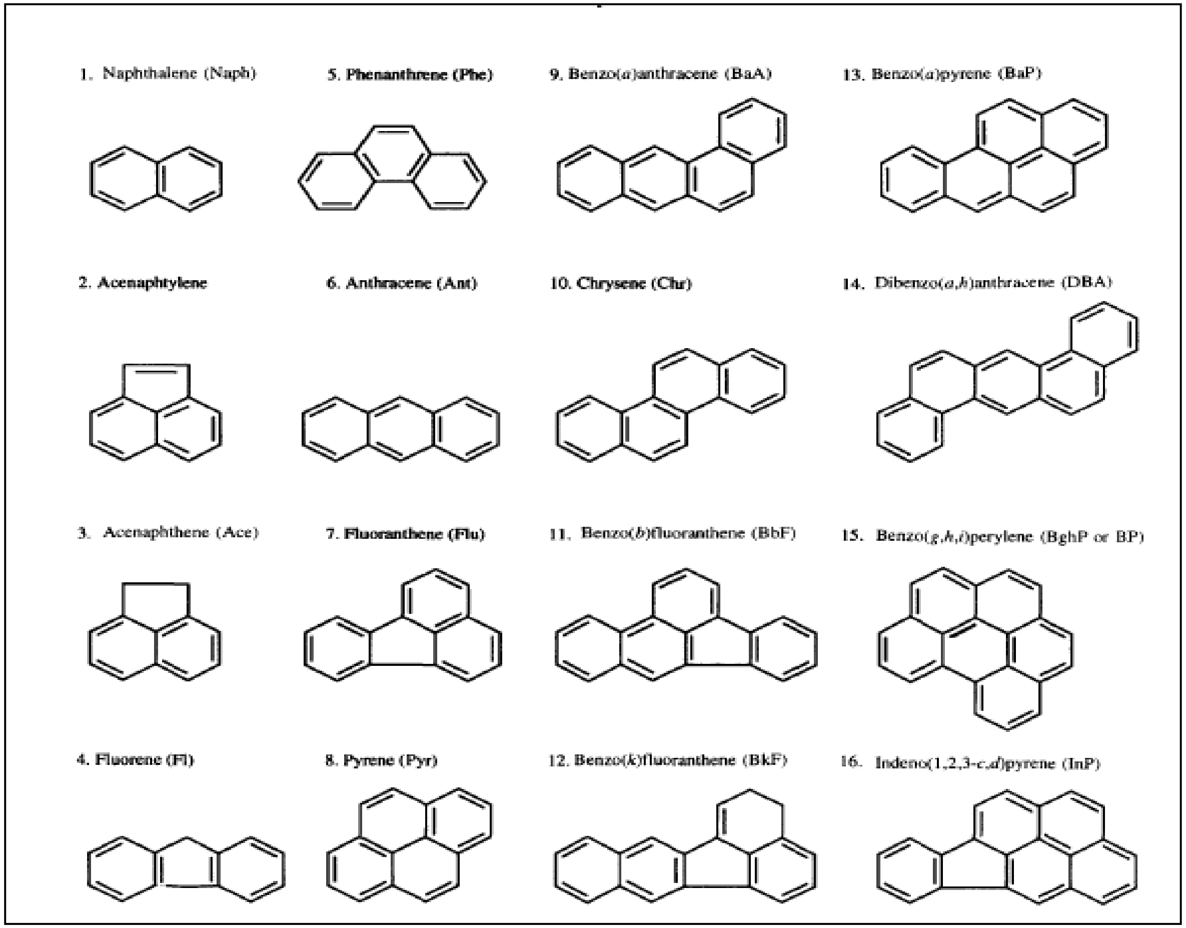

chrysene


benzo(g,h,i)perylene

https://en.wikipedia.org/wiki/Polycyclic_aromatic_hydrocarbon

Polycyclic aromatic hydrocarbons (PAHs)

Structures of US EPA's 16 priority PAH pollutants



Screening analysis shown peaks representing other species

Target – determination of unknown species GC

SAMPLING

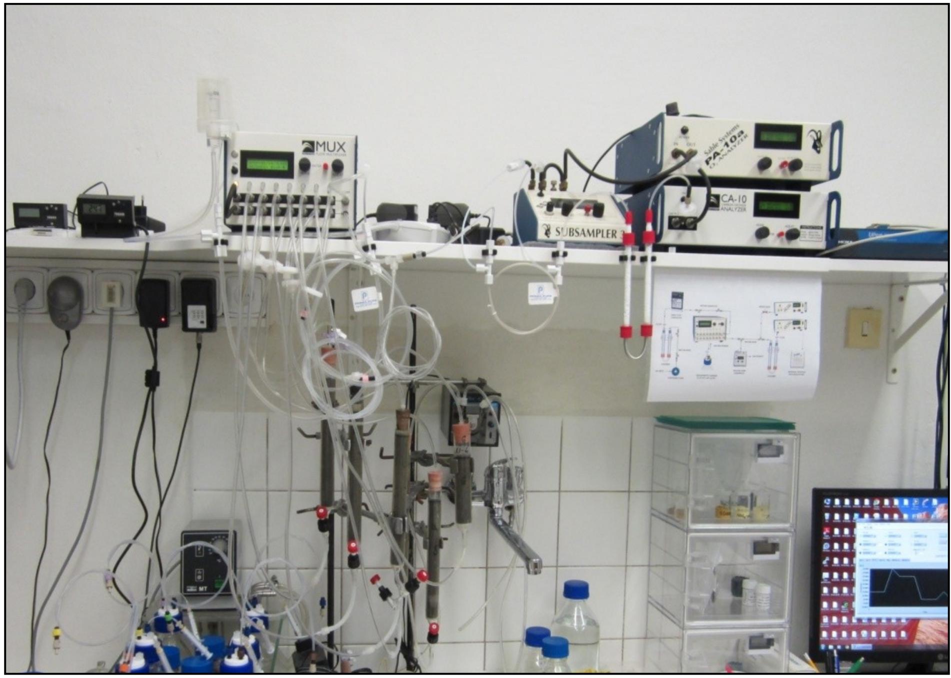
- Soil sample was collected from the storage area of wooden railway sleepers impregnated by oil preservatives (30 years of activity) - creosote, coal tar, asphalt, petroleum and other bituminous materials

- geological profile consists of a coarse gravel with sand, loam and clay sediments up to a depth of 2.6 to 3.1 meters and finally gravel fluvial sediments. The groundwater level is located at a depth of about 4.5 m.

- The air dried soil sample was ground, mixed thoroughly and passed through a 2-mm sieve to remove gravel and debris

Bioremediation - POPs

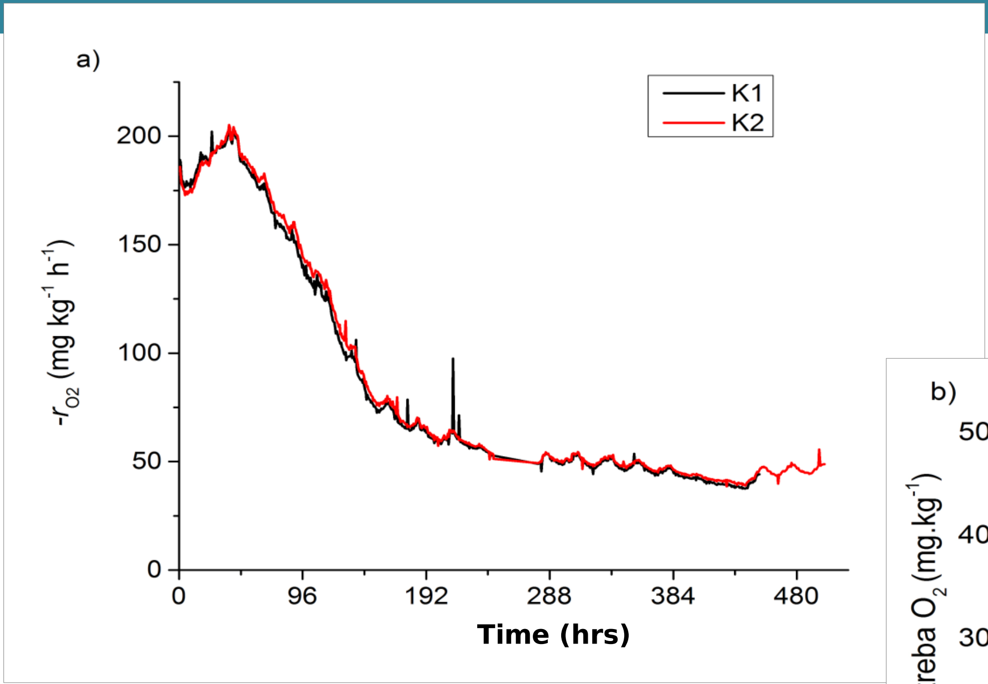
Glass columns filled with contaminated soil



Respiratory system

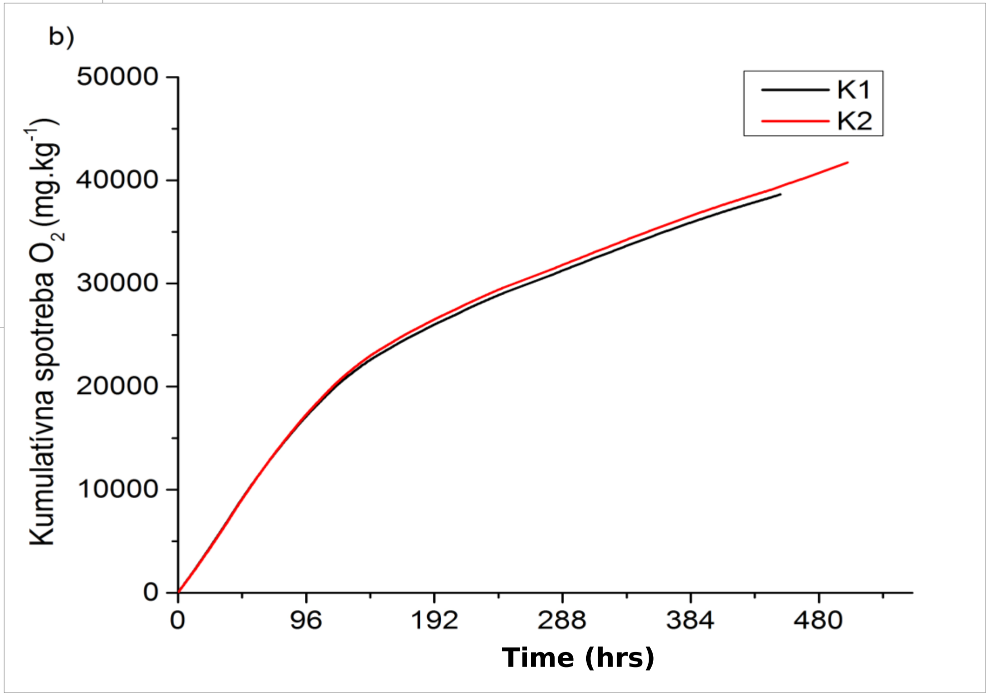
indigenous microorganisms

Bioremediation – aerobic, 20 days



indigenous microorganisms

b) Cumulative amount of consumed O_2



a) Degradation rate of O_2 consumption

- Maximum degradation rate was achieved within 2 days, then the rate slowly decreased
- Significant rate decrease – first 10 days (from 200 mg O_2 kg^{-1}.h^{-1} to 61 mg O_2 kg^{-1}.

After 20 days – CO_2 production (approx 40 g.kg^{-1} dried soil) showed that the mineralisation was equivalent to 10 g.kg^{-1} TOC

Determination of PAHs in soil

Soil sample preparation includes:

- **Pretreatment** - air drying, sieving, homogenization
- **Extraction** - Soxhlet extraction
- **Clean up** - Solid Phase Extraction (SPE)
- **Analysis** - High Performance Liquid Chromatography with a Diode Array Detector (HPLC-DAD)

Soxhlet extraction and SPE

- 5 g of dry soil + 5 g of anhydrous sodium sulfate
- extraction was performed for 20 h with 150 ml of petroleum ether

- Chromabond CN/SiOH column
- column conditioning with petroleum ether
- aspiration of the extract through the column under vacuum
- column washing with petroleum ether
- the elution with acetonitrile/ toluene (3:1)

  the evaporation to dryness with a gentle N_2 current and vacuum

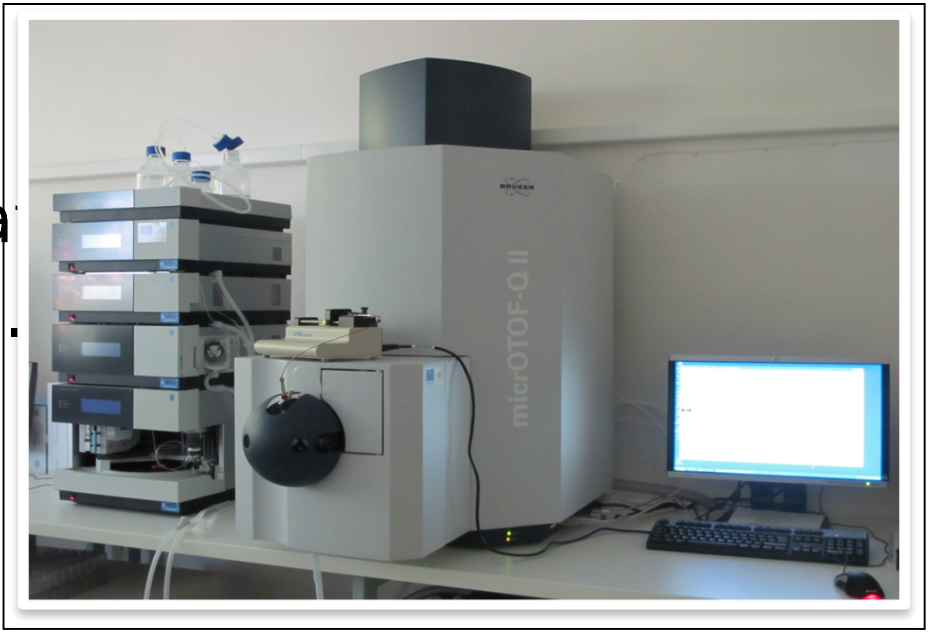
HPLC analysis

- Separation of the 16 PAHs was performed with a column 250 x 3 mm Nucleosil 100-5 C18 PAH.
- Elution was carried out with mobile phase flow rate of

  0.5 ml/min at a controlled oven temperature of 25ºC.
- The sample injection

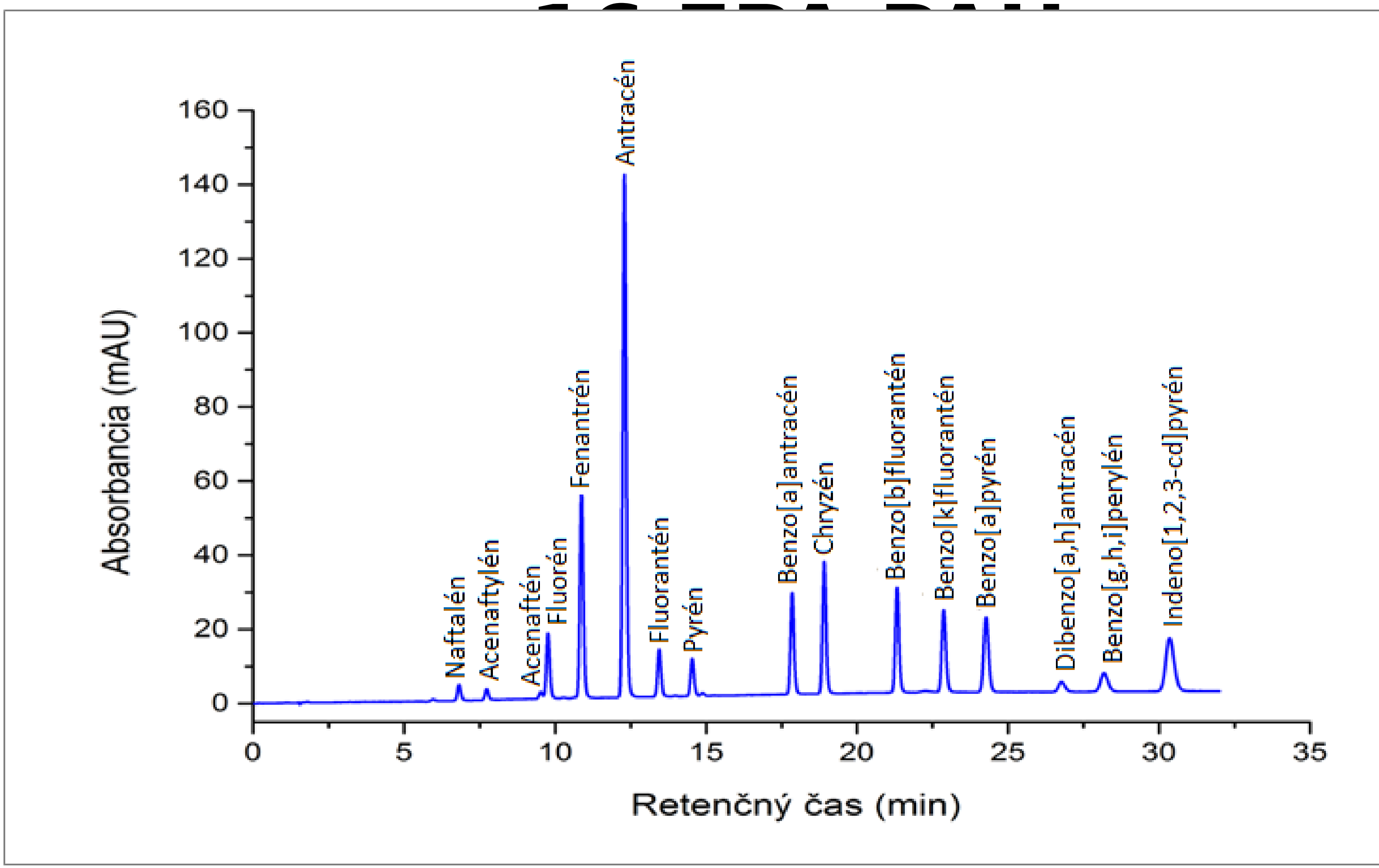
  volume was 10 µl.
- The detector was used at

  the wavelength 254 nm.



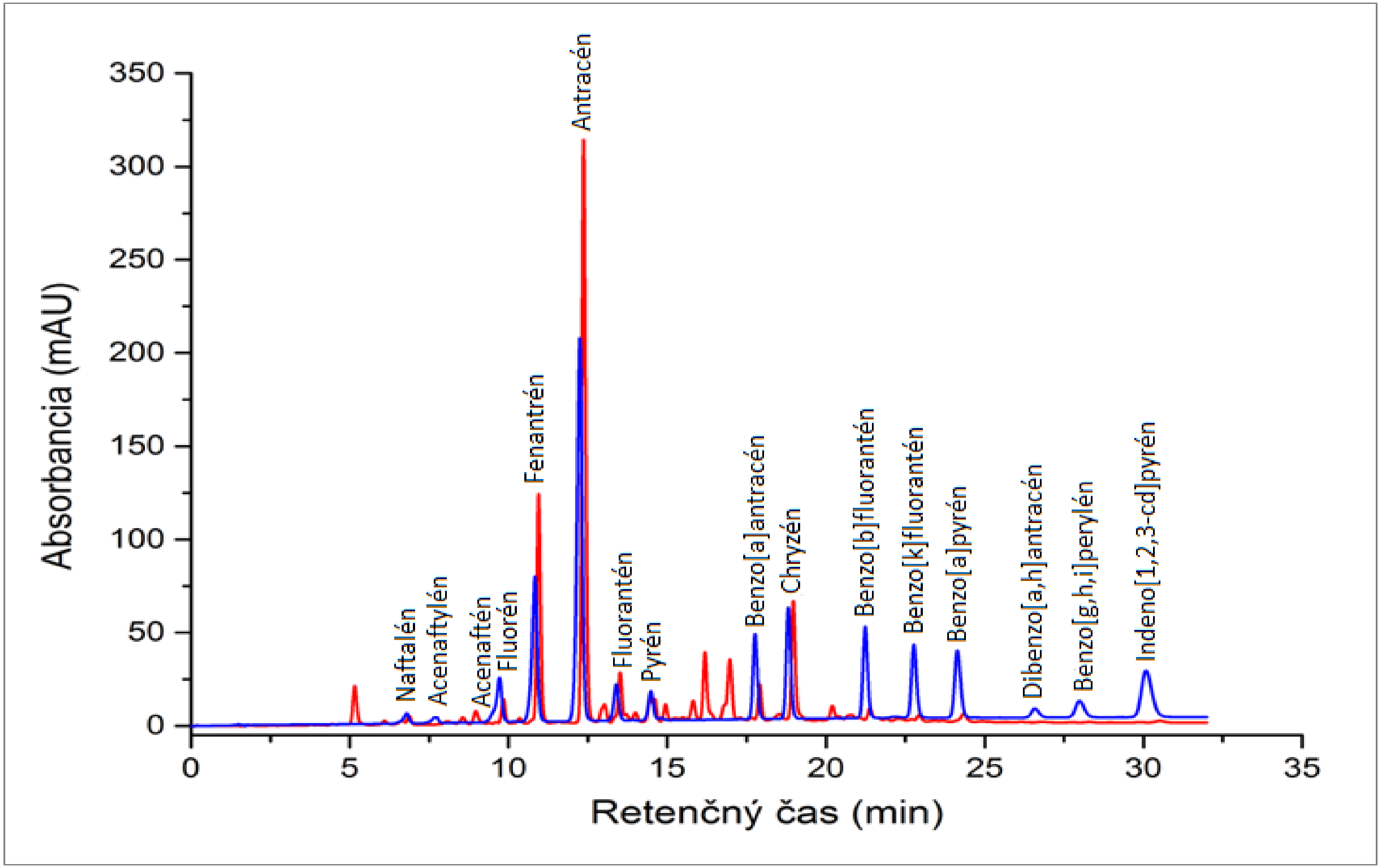
UHPLC Dionex Ultimate 3000 a MS spektrometer Bruker MicrOTOF QII

HPLC analysis of standard mixture



concentration 2 μg.ml^{-1}

Analysis of real sample



Comparison of chromatograms – standard and extract of rereal sample

HPLC analysis

Table 2. The concentrations of 16 selected EPA PAHs in soil sample during degradation

PAH (number of rings)	PAH concentrations (mg kg^{-1})	
	0 days	20 days
Naphthalene (2)	3035.33	2472.85
Acenaphthylene (3)	n.a.	n.a.
Acenaphthene (3)	879.06	1625.79
Fluorene (3)	1822.71	1282.70
Phenanthrene (3)	5567.08	3982.37
Anthracene (3)	6023.37	5579.26
Fluoranthene (4)	5521.28	5291.26
Pyrene (4)	2899.07	2616.95
Benzo[a]anthracene (4)	1694.77	1494.05
Chrysene (4)	4583.45	3896.54
Benzo[b]fluoranthene (5)	687.39	622.67
Benzo[k]fluoranthene (5)	400.68	351.83
Benzo[a]pyrene (5)	601.92	517.69
Dibenz[a,h]anthracene (5)	352.36	220.26
Benzo[g,h,i]perylene (6)	145.16	97.68
Indeno[1,2,3-cd]pyrene (6)	140.03	120.80
Sum of PAHs	**34353.66**	**30172.70**

Conclusions

- The amount of 16 selected PAHs converted to total carbon decreased by 4 630 mg kg^{-1}.
- Other organic substances, polyaromatic compounds not monitored within the 16 US EPA PAHs and their derivatives are present in the soil.
- These compounds can be transformed into lower molecular weight compounds (including EPA PAHs) by cleaving a portion of the molecule by bacteria.
- **indigenous microorganisms** should be considered as a potential method for biodegradation.

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