

# WP4 Final deliverables D.4.1.1., D.4.1.2., D.4.1.3

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## Introduction

### **PEPSEA | PP1 - Consorzio Futuro in Ricerca (CFR)**

This document is related to the following deliverables:

- D.4.1.1. Technological solution for sea pollution cleaning developed
- D.4.1.2. Polygon for testing the technological solution for sea pollution cleaning established
- D.4.1.3. Technological solution for sea pollution cleaning tested

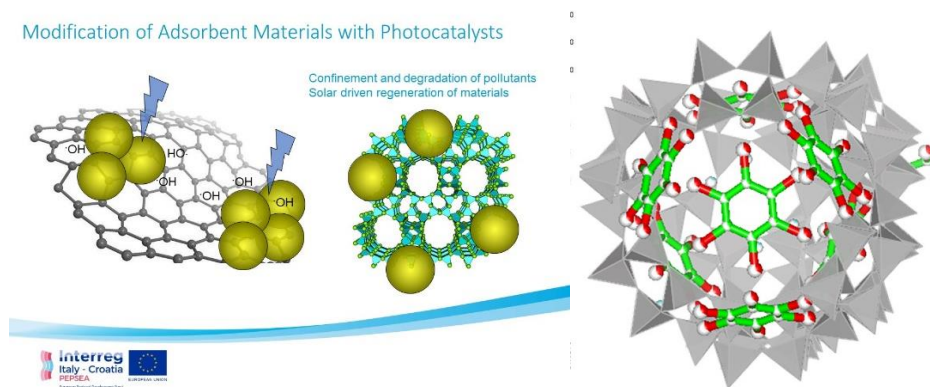
Regarding the activities foreseen by PEPSEA project, CFR was relied on the Unit of the department devoted to water remediation based on advanced oxidation process (where wide band gap semiconductors are used as light harvesting materials to drive thermodynamically demanding oxidation processes for the removal of water contaminants) as well as on adsorption of emerging pollutants by porous materials. All experimental data were carried out in laboratories equipped with technical instrumentation:

- GC/MS and HPLC/MS Gas and Liquid chromatography/mass spectrometry
- HPLC/ICP/MS liquid chromatography coupled with inductively coupled plasma and mass spectrometry
- X-ray Powder diffraction
- Thermal Analyses (TG, DTG, DTA)
- UV-Vis spectroscopy and Fluorescence scanning microscopies (SEM, AFM)
- Photoelectrochemistry and transient optical spectroscopy

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#### D.4.1.1 Newly developed technological solution

Petroleum-based products are among the most widespread environmental pollutants, their presence is mainly due catastrophic accidents and chronic pollution. In particular, the Mediterranean Sea is one of the most congested basins in terms of oil tanker traffic and this made several coastal ecosystems constantly exposed to severe hydrocarbons contaminations. Indeed, some marine coastal area of the Mediterranean Sea have been identified as a chronically polluted with heavy industrialization (petrochemical and wastewater treatment plants) and the presence of a commercial harbour. The possibility to have available effective techniques to successfully remedy HC-contaminated marine environments is essential for environmental and economic sustainability as well as human health. Recently, it has been shown that hydrophobic zeolites are environmentally compatible materials, which have been efficiently employed as adsorbents for the removal of emerging organic contaminants from water bodies. Their adsorption capacity, shape-selectivity, chemical stability, mechanical strength, no salt interference - along with their high availability and low-cost - make these sorbents as very promising tools for dealing with water contamination.

##### Adsorption of organic contaminants: effect of co-contamination

With this purpose the WP4.1 research activity has concerned the evaluation of the adsorption properties of different adsorbent materials with respect to two organic compounds, selected as representative of the chlorinated and aromatic class of hydrocarbons. As adsorbent material ZSM-5 and Y zeolite, commercially available, were selected. The zeolite Y (FAU topology) is a large pore material with large cavities joined to four others via 12 membered-rings (MR) of tetrahedral, whereas ZSM-5 is a medium-pore zeolite characterized by two intersecting sets of tubular channels: a sinusoidal 10MR channel parallel to the [010] direction and a straight 10MR channel parallel to the [100] direction. High-silica Y (code HSZ-390HUA, 200 SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, 750 m<sup>2</sup>/g<sup>-1</sup> surface area, 0.05 wt. % Na<sub>2</sub>O content) and ZSM-5 (code CBV 28014, 280 SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio, 400 m<sup>2</sup>/g<sup>-1</sup> surface area, 0.01 wt. % Na<sub>2</sub>O content,) hydrophobic zeolites were purchased in their as-synthesized form by Tosoh Corporation (Japan) and Zeolyst International, respectively. The adsorption isotherms and kinetics of both Toluene (TOL) and Chlorobenzene (CB) on zeolite Y have been already obtained by some of us (Catal. Today, 277 (2016) 118-125. <https://doi.org/10.1016/j.cattod.2015.11.031>). However, these compounds when present in aqueous mixture could compete in the adsorption. Since in many cases marine environments are polluted by a large variety of contaminants, the removal ability of zeolites with respect of mixtures of contaminants should be also evaluated.

The adsorption isotherms of TOL-CB mixture on Y zeolites and ZSM-5 are reported in Figures 1 and 2 respectively.

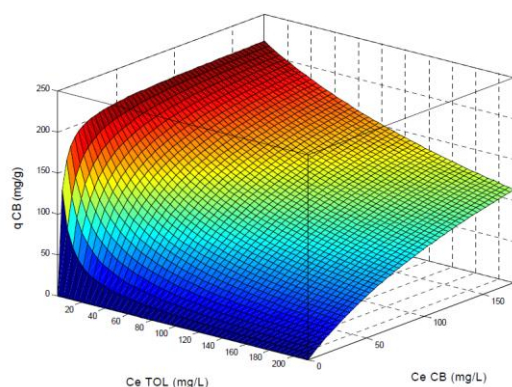


Figure 1: Adsorption isotherms of TOL-CB mixtures in aqueous solution onto Y zeolite

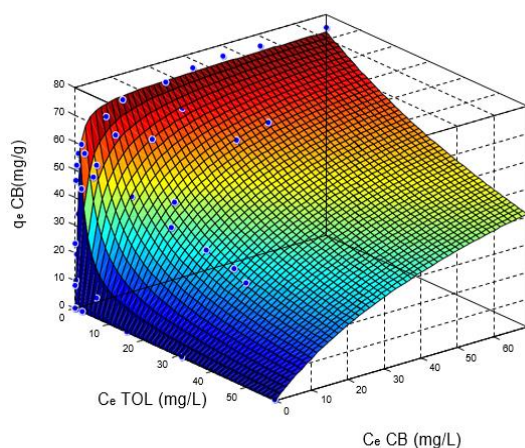


Figure 2: Adsorption isotherms of TOL-CB mixtures in aqueous solution onto ZSM-5 zeolite

To investigate more in detail this behavior, the adsorption of CB from mixture containing a fixed amount of CB and variable concentration of TOL were measured (see Figure 3). It can be seen that competitive adsorption occurs for both the studied materials thus indicating that possibly CB and TOL are adsorbed on the same adsorption site of the zeolites.

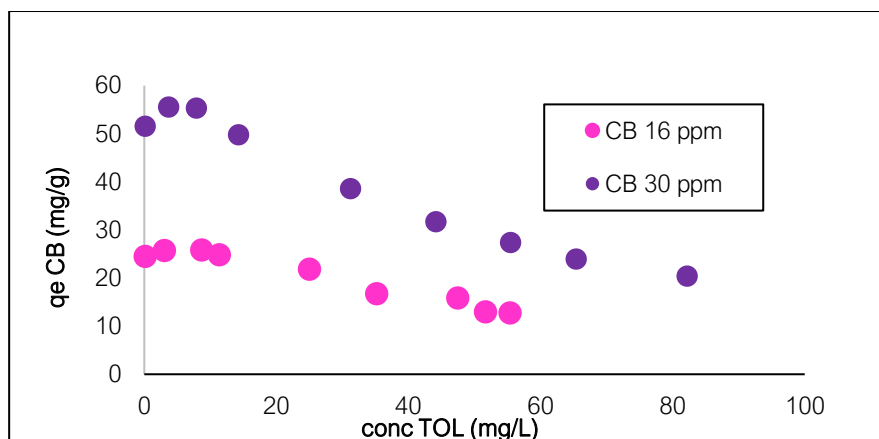


Figure 3: Adsorbed quantity of CB onto ZSM-5 vs. the initial concentration of TOL in solution.

The adducts of zeolite and binary mixture of the selected pollutants are also investigated by a structural approach in order to get a better understanding of the geometrical arrangement of adsorbed molecules and their chemical environment in the zeolite pores to understand the functionality of the host-guest interactions between TOL/CB and zeolites. The insights gained from structural refining has been employed as input of the competitive adsorption modelling. The present combined approach of integrating structural information to thermodynamic equilibrium data is an excellent model system for realistically describing the adsorption process and helping in the interpretation of the adsorption mechanisms (Figure 4).



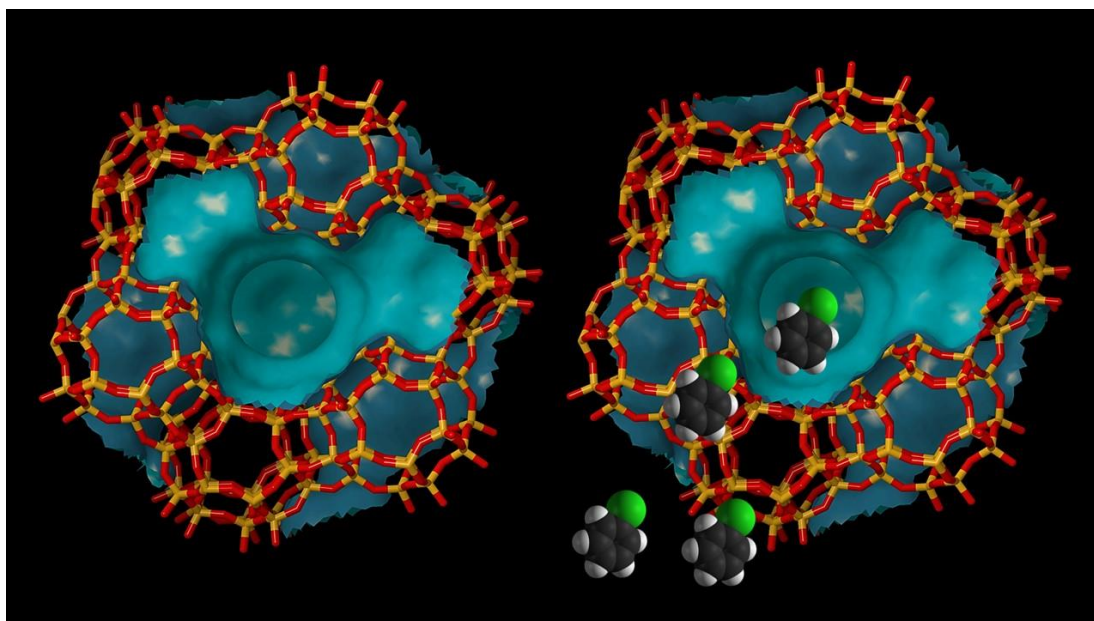


Figure 4. Adsorption of CB in the zeolite pores.

The total weight loss obtained for the sample of ZSM-5 loaded with the mixture is about 13% in very good agreement with the results obtained through the adsorption analysis. As reported by DTA curves, the expulsion of contaminants is accompanied by an exothermic reaction (Figure 5). According to adsorption analysis, thermal measurements indicate that both TOL and CB are incorporated in ZSM-5 in a comparable amount.

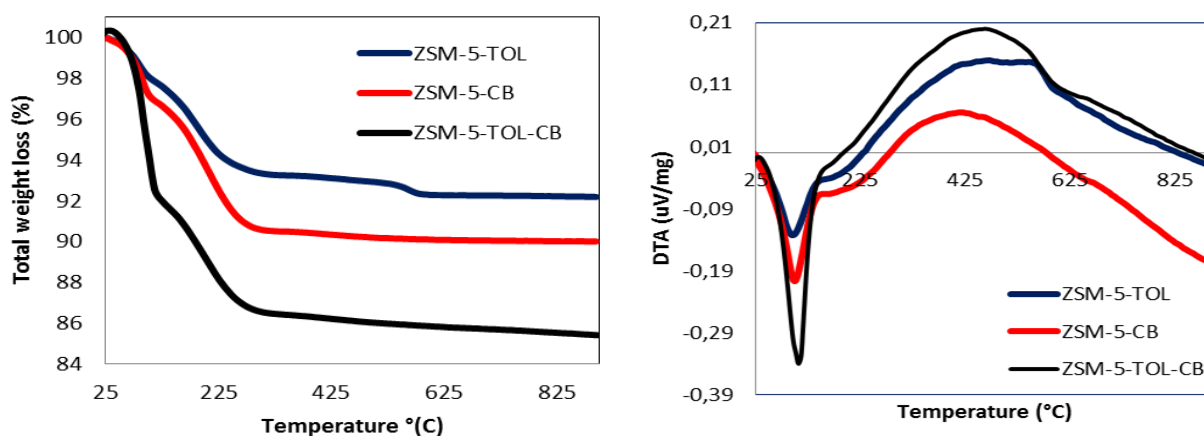


Figure 5. TG and DTA curves after adsorptions of toluene (blue line), chlorobenzene (red line) and mixture of them (black line) in ZSM-5

After TOL-CB mixture adsorption, the evolution of the powder diffraction pattern highlights that ZSM-5 maintains its crystallinity also after mixture adsorption. In particular, in the diffraction pattern of loaded ZSM-5 a variation of peaks intensity and position along the investigated  $2\theta$  range suggests a change in the lattice parameters and in the hosted extraframework species (Figure 6).

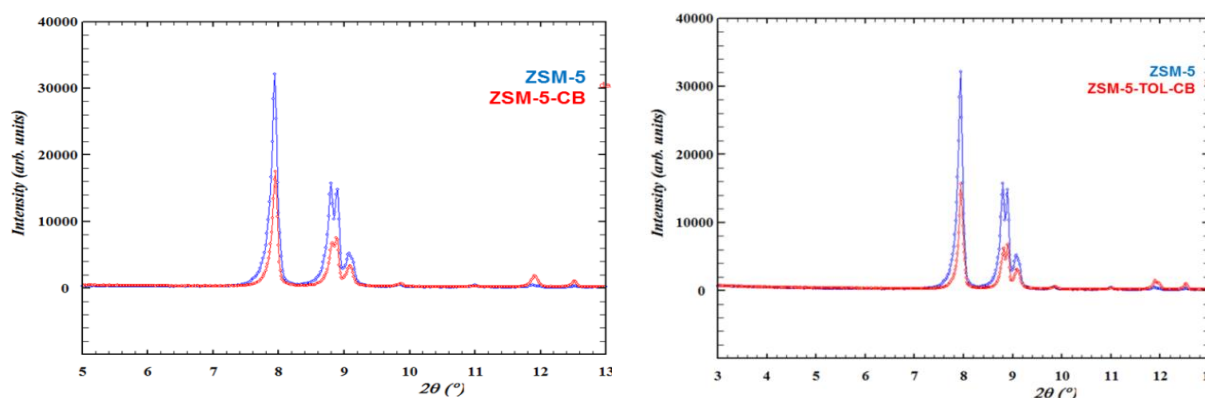


Figure 6. XRD powder pattern diffraction of ZSM-5 loaded with toluene, chlorobenzene and mixture of both organics. Unloaded ZSM-5 pattern (light blue line) are also reported for comparison.

In particular, based on the refined distances a strongly interaction of water-toluene and water-chlorobenzene oligomers with the framework oxygen atoms occurs thus guaranteeing the immobilization of both pollutants in the zeolite porosities. Moreover, according to adsorption results, refined occupancies confirm the strong and similar affinity of ZSM-5 for both TOL and CB observed through adsorption isotherms.

Since competitive adsorption can occur, natural organic matter can interfere in the contaminants adsorption from aqueous solution. In general, humic substances, characterized by relatively high molecular weight have dimensions larger than the zeolite opening windows, and should not significantly affect the adsorption of contaminants. However, small molecules belonging to the wide class of natural organic matter such as allelochemicals or phenol lignin derivatives have dimensions that make them suitable for adsorption into the porous structure of a variety of synthetic zeolites. It is therefore important to evaluate the possible interaction of phenol lignin derivatives with zeolites to evaluate the potential effects arising in the application of zeolite to improve groundwater or soil quality contaminated by VOCs.

The competitive adsorption of mixture of Toluene (TOL) and CA in a wide concentration range was evaluated. In addition, the effects of aqueous chemistry characteristics (i.e. pH and ionic strength) is also considered. To accomplish this task, adsorption isotherm of both zeolite resulting from the adsorption of unary and binary mixtures were evaluated. To explore the possible interaction

between CA, TOL, potential solvent molecules (water) and the zeolite framework, a structural investigation was carried out to localize the molecules inside the porous structure of the zeolite.

Sorption isotherms of CA on ZSM-5 at different pH values are shown in Figure 7. It can be noticed that in acidic condition there is an appreciable adsorption of CA on ZSM-5, whereas on zeolite Y the CA adsorption was negligible in the investigated pH range. This discrepancy can possibly arise from the difference in the microporous structure of the two zeolites compared to the CA molecular dimension. Indeed, it has been observed that the adsorption from dilute solution is more efficient for zeolites having cavities and channels with dimensions close to that of the host. Additionally, this trend is observed at different concentration and it can be noticed that for high concentration of CA in solution a modest adsorption on ZSM-5 occurs even at pH close to neutral condition. This finding indicates that in solution containing a large amount of natural organic matter, and such as phenolic derivatives, adsorption competition with organic pollutants on zeolites can occur.

It can be seen in Table 1 that both adsorption constant  $b$  and saturation capacity are lower for caffeic acid than those previously obtained for toluene, indicating a higher affinity of ZSM-5 for toluene molecule (roughly 8.55 % in weight analyses).

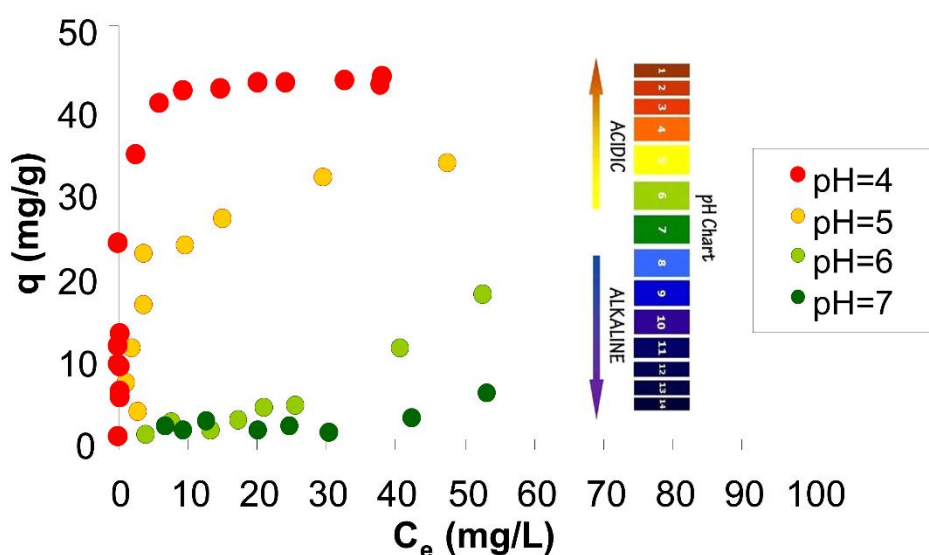


Figure 7: Adsorption isotherms of caffeic acid in aqueous solution onto ZSM-5 zeolite

**Table 1.** Langmuir model parameters obtained by non-linear fitting of TOL-CA binary mixtures adsorption data at pH=5 (see Fig. 7) Confidence limits at 95% of probability are reported in brackets.

				R <sup>2</sup>
ZSM-5-TOL-CA	TOL	q <sub>S</sub> (mg g <sup>-1</sup> )	81 (75, 88)	0.9661
		b <sub>TOL</sub> (L mg <sup>-1</sup> )	2.51 (2.29, 2.73)	
		b <sub>CA</sub> (L mg <sup>-1</sup> )	0.21 (0.16, 0.26)	
	CA	q <sub>S</sub> (mg g <sup>-1</sup> )	39 (34, 44)	0.9474
		b <sub>CA</sub> (L mg <sup>-1</sup> )	0.18 (0.11, 0.25)	
		b <sub>TOL</sub> (L mg <sup>-1</sup> )	2.60 (2.34, 2.87)	

Thermogravimetric analysis was performed to gain information on the thermal regeneration of ZSM-5 saturated with CA, and to evaluate the main degradation by-products that can be generated during the heating of this material.

Thanks to the ZSM-5 thermal stability, zeolites can be thermally regenerated, and it has been demonstrated that the saturation capacity of the regenerated sample after air calcination does not significantly differ from that of fresh material [29]. Fig. 8 reports differential thermal analysis (DTA) and thermogravimetric (TG) curves of a pure caffeic acid (CA) (Fig. 8a) and of the adduct CA-ZSM-5 (see Fig. 8b) respectively. TG analysis revealed that in CA-ZSM-5 three thermally degradations main steps are recognized. The first one proceeds in the range from room temperature to ≈100 °C and can be related to the release of both species (waters and/or caffeic acid molecules) weakly bonded to the zeolite surface. Then the ZSM-5-CA TG profile shows a sudden weight loss rated at 250 °C for the second stage, very similar to that detected in the CA pure sample. In the literature it was reported that this stage of weight loss (210–240 °C) corresponds to partial thermal decomposition of caffeic

acid with the formation of volatile pyrolysis products such as ion of 3,4-dihydroxy-phenylethylene. The decomposition/desorption process continues in a wide temperature range (250–550 °C) with the release of CO<sub>2</sub>. In CA-ZSM-5 this process gives rise to a wide exothermic DTA curve (Fig. 8b) suggesting firstly the relaxation of co-adsorbed water and, consequently, the presence of the host-guest interactions (also mediated by water) involving the CA carboxylic group and the zeolite framework. Then CA decomposition stage, giving the formation of volatile products, continues and their desorption finishes at ≈630 °C (Fig. 8a).

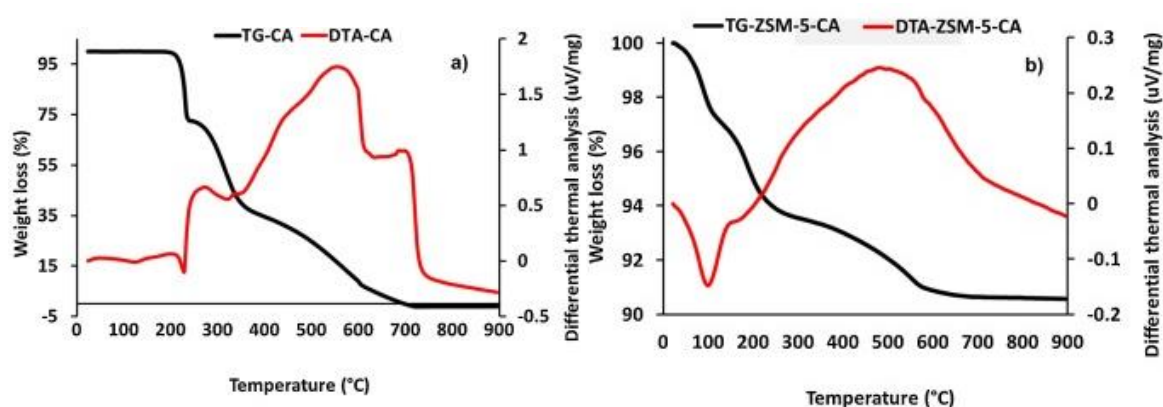


Fig. 8. Simultaneous Thermogravimetry (TG) and Differential Thermogravimetry (DTG): a) pure CA, and b) ZSM-5-CA in the temperature range 25–900 °C. (<https://doi.org/10.1016/j.ijece.2020.104229>)

The location of CA determined by diffractometric analysis using Rietveld structure refinement was reported in Fig.9.

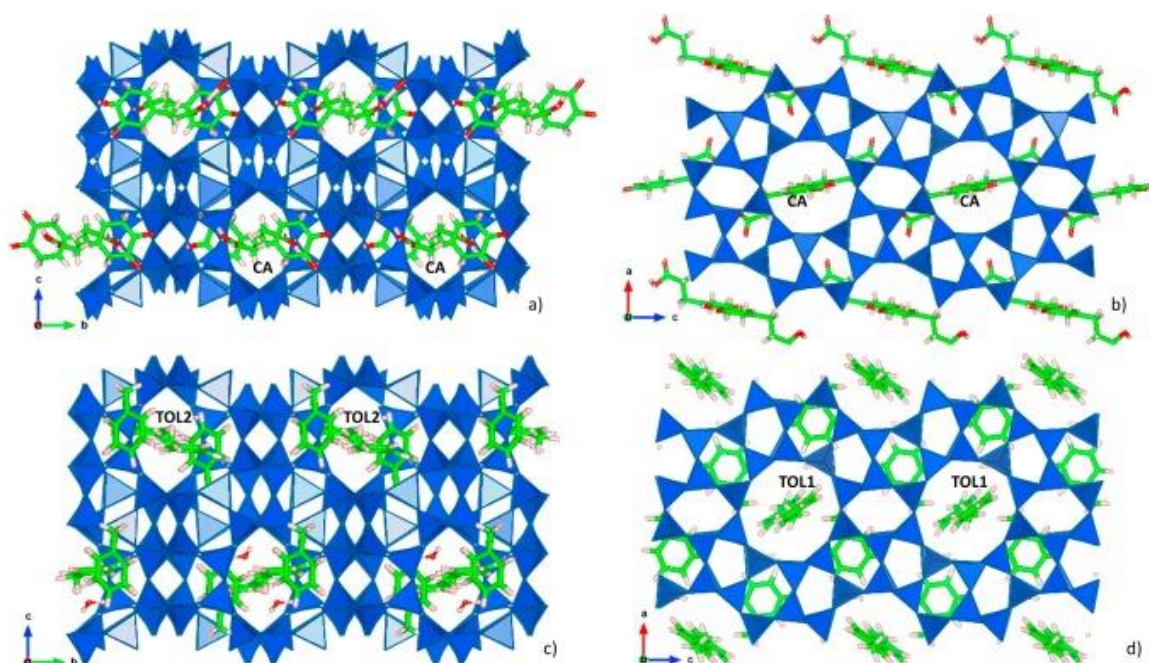


Figure 9. Rietveld structure refinements of ZSM-CA system: adsorption sites of CA in ZSM-5 structure along a) (100) and b) (010) axis, respectively. The corresponding adsorption sites of TOL in ZSM-5 along c) (100) and d) (010) axis, respectively were also reported for comparison. (<https://doi.org/10.1016/j.jece.2020.104229>).

### Testing of adsorbent materials: preconcentration media.

The adsorption capacities of two Faujasite topology zeolites with Silica/Alumina Ratio 30 and 200 were evaluated using as probe molecules ketoprofen, hydrochlorothiazide, and atenolol. These last were selected, because of their occurrence in surface waters and effluents from wastewater treatment plants. The selected zeolites were demonstrated to be efficient sorbents towards all investigated pharmaceuticals, thanks to their high saturation capacities (from 12 to 32%w/w) and binding constants (Figure 10). These results were corroborated by thermal and structural analyses, which revealed that adsorption occurred inside zeolite's porosities, causing lattice modifications (Figure 11).

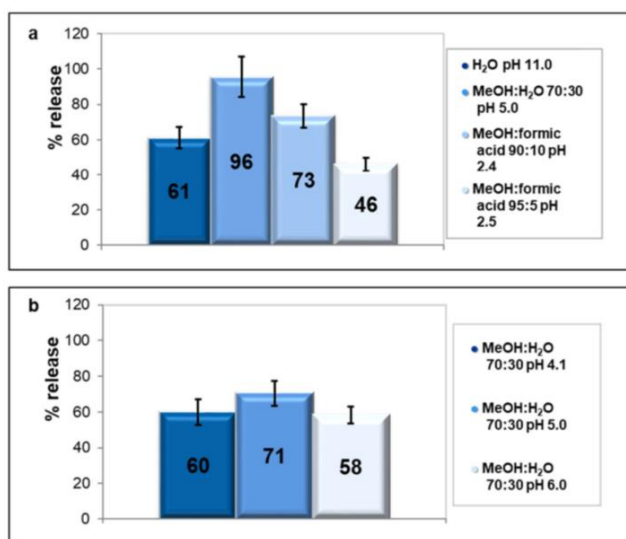


Fig. 10 Release of HCT 1 mg/L from Y200 with different extracting phases (a) and from Beta25c with mixture MeOH:H<sub>2</sub>O 70:30 at different pH (b).

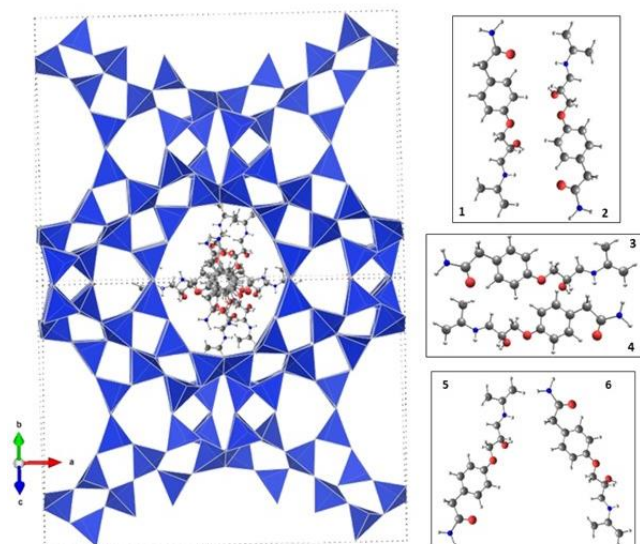


Figure 11. Rietveld structure refinements of zeolite Y after adsorption sites of atenolol.

In addition, zeolites have been tested as a pre-concentration media in the dispersive-solid phase extraction procedure. Recoveries higher than 95% were gained for ketoprofen and hydrochlorothiazide and approximately 85% for atenolol, at conditions that promoted the dissolution of the neutral solute into a phase mainly organic. The results were obtained by using a

short contact time (5 min) and reduced volume of extraction (500  $\mu$ L), without halogenated solvents. These appealing features make the proposed procedure a cost and time saving method for sample enrichment as well as for the regeneration of exhausted sorbent, rather than the more energetically expensive thermal treatment.

Monodirectional zeolites like zeolite L and ZSM-12 were analysed after thermal activation, because in mono-directional pores, molecules diffusing in the channel have to move one after the other following the same direction and can be easily blocked. Combined separation techniques, neutron and X-ray powder diffraction techniques were used and the obtained information are crucial to tailor the physicochemical properties of zeolites as well as to address their hydrophobicity, pore dimensions and cavities thus optimizing the selectivity of zeolite adsorbent.

### Develop, characterization and testing a green and scalable photocatalyst capable of degrading organic pollutants under sunlight illumination

To the end of developing a green and scalable photocatalyst preparation method we have searched for hydrothermal syntheses where water is the only solvent. Among many methodologies for the preparation of WO<sub>3</sub> based photocatalyst we consider the hydrothermal/solvothermal approach the favorite one for the scalable functionalization of different substrates with a photocatalytic coating having good mechanical stability. Most of the hydrothermal routes lead to different morphologies, hence photocatalytic efficiencies, depending on the details of the precursor composition. Among relevant literature we have explored the approach of Lin et al (J.Am.Chem.Soc. 2018, 140, 9078–9082) which proposes two variants of hydrothermal crystal growth, where the presence of a directing agent leads to the formation of either WO<sub>3</sub> nanosheets or nanowires. Different structures imply different crystal facets orientation which has consequences on the charge separation and transport efficiency. We have however considered a modified procedure, inspired by Wang et al. (Nano Energy 24 (2016) 94–102) which consists in a two step material growth, each of the duration of 8 hours, which is endowed by a good reproducibility and affords a substrate with good photoelectrochemical performance and good porosity (Fig. 12 (a,b)) for (photo)electrochemical reactions in aqueous medium. We have verified that depending on the crystal seed layer one can fabricate multi-nanoplates which assemble in large prismatic structures (Fig.12, (a)), or smaller nanoplates (ca. 300 x 300 nm) giving rise to roughly vertically aligned pillars. Both morphologies display good photon to electron conversion which is ca. 70% that of the WO<sub>3</sub> nanoflakes built in organic solvents. A good result considering that this preparation route does not involve toxic chemicals.



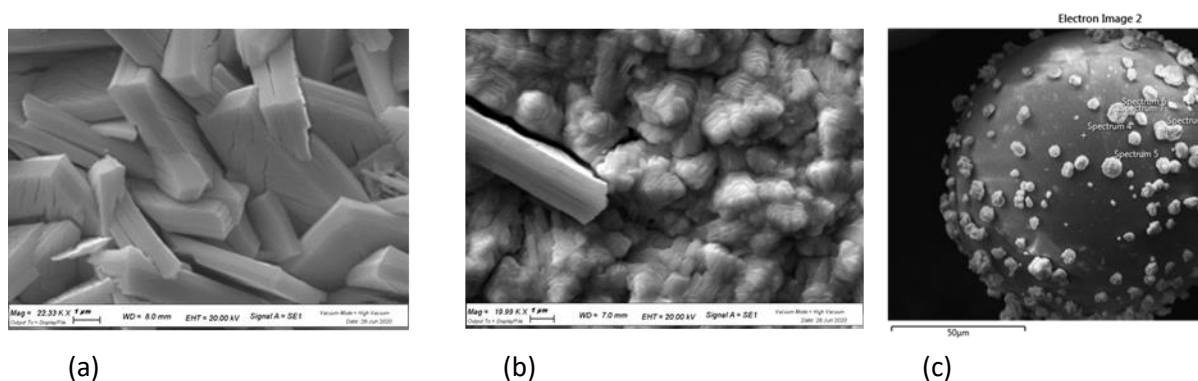


Fig. 12 SEM microscopy of  $\text{WO}_3$  photocatalysts fabricated on planar substrates with different crystal seed layers (a) and (b) and deposited on  $\text{SiO}_2$  microspheres (c).

We have verified that the  $\text{WO}_3$  deposition can be performed on different inert substrates, which provides a physical support for the photocatalyst, including adsorbent phases or spherical glass beads. We have initially considered  $\text{WO}_3$  growth on 4 mm spherical beads, which visually resulted in a good and homogeneous coating of the glass substrate. In order to increase the active area, we have tested the hydrothermal deposition also on quartz microspheres (ca.  $125\mu\text{m}$  diameter) where the deposition of the photocatalyst was evidenced by SEM and EDS analyses. SEM imaging (Fig.13 (c)) reveals the presence of microscopic  $\text{WO}_3$  aggregates having  $1\text{-}10\mu\text{m}$  size, where the W EDS signals are particularly strong (82 % Wt tungsten). However, also the apparently uncovered smooth surface of the sphere, where aggregates are not noticeable, are covered by active material, probably in the form of a very thin (few nm thick) featureless  $\text{WO}_3$  film, as shown by the weak W emission in EDS spectra of Fig.13 (a). We have also preliminarily observed that this synthetic route can be exploited to modify high surface area silica or carbon based adsorbent materials.

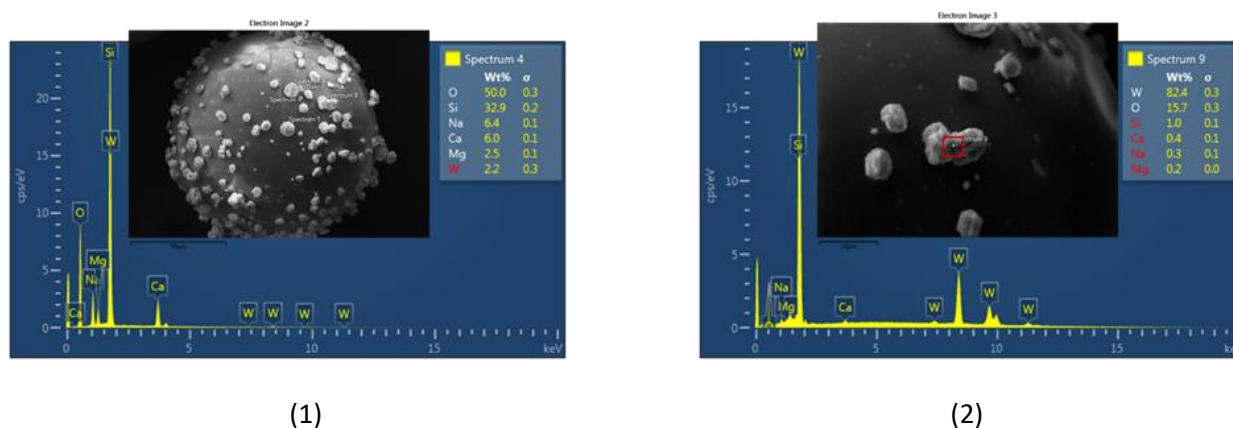


Figure 13. EDS analyses of different portions of the coated bead surface. (1) smooth region; (2) aggregate.

Finally, we have been working to improve the intrinsic photocatalytic efficiency of  $\text{WO}_3$  in environmental remediation applications. We have explored the coupling of  $\text{WO}_3$  with silver oxide, that we deemed a good hole transfer co-catalyst for the oxidation of organic species. We have explored the activity of  $\text{WO}_3/\text{Ag}_2\text{O}$  (W/Ag) composites, obtained by co-precipitation followed by calcination, in the presence of methyl orange (MO) dye as a model organic pollutant.

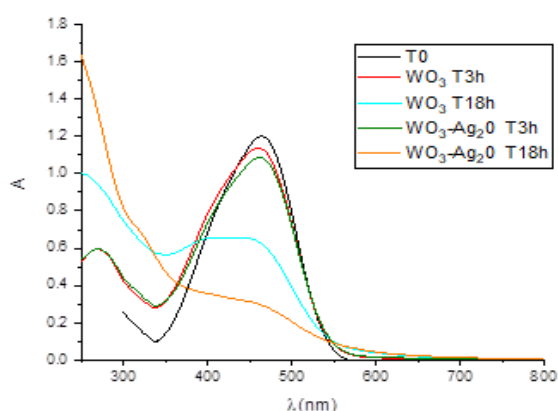


Figure 14. Photodegradation of MO as an organic model pollutant in the presence of  $\text{WO}_3$  based catalysts

Photooxidation tests performed with a Xe lamp equipped with a water filter and a 360 nm cut-off on a 0.05 mM MO solution show that the W/Ag material leads, upon ca. 7 hour illumination, to a substantial decrease (ca.50%) of MO absorption, consistent with dye photodegradation. By comparison, with pure  $\text{WO}_3$  the dye degradation is quite marginal (ca.10 %). 18 hour illumination tests reveal a nearly 70% abatement of MO whereas MO alone (without  $\text{WO}_3$  based catalysts) does not undergo a substantial photodegradation under the same illumination conditions (Figure 16).

The typical structure of solvothermal  $\text{WO}_3$  grown on top of the adhesion layer is characterized by a homogeneous coverage by  $\text{WO}_3$  leafs and lamellae (Figure 15), roughly vertically aligned with respect to the surface and arranged in somewhat organized superstructures which may resemble flowers or flakes. These leafs are relatively thin ( $< 100$  nm) compared to their length and width which extend for several microns. A closer inspection of the cross section of the electrode reveal the presence of different features and discontinuities in the layered structure. Immediately on top of the compact  $\text{WO}_3$  seed layer, there is a region having a thickness of few hundreds nm which is composed by disordered nanoparticles whose diameter range between 50 and 100 nm. This sort of debris, probably produced during the early stage of the solvothermal growth, is covered by the lamellar layer (about  $8 \mu\text{m}$  thick) which is clearly where most of the photon absorption and scattering will occur.

X-ray diffraction (XRD) data (Figure 13) confirmed that the film is composed to by high-quality monoclinic  $\text{WO}_3$ , with P 21/n space group, formed during high temperature annealing with Cell parameters of  $a=7.320\text{\AA}$ ,  $b=7.518\text{\AA}$ ,  $c=7.670\text{\AA}$  ( $V(\text{\AA}^3)=422.1$ ),  $\beta=90.4^\circ$  ( $\text{WO}_3$  database code ICSD 80056) Crystallite size of in the film is much smaller than the size of a whole lamella, being only 25.09 nm. Thus every leaf is formed by several nanometer sized  $\text{WO}_3$  crystallites.

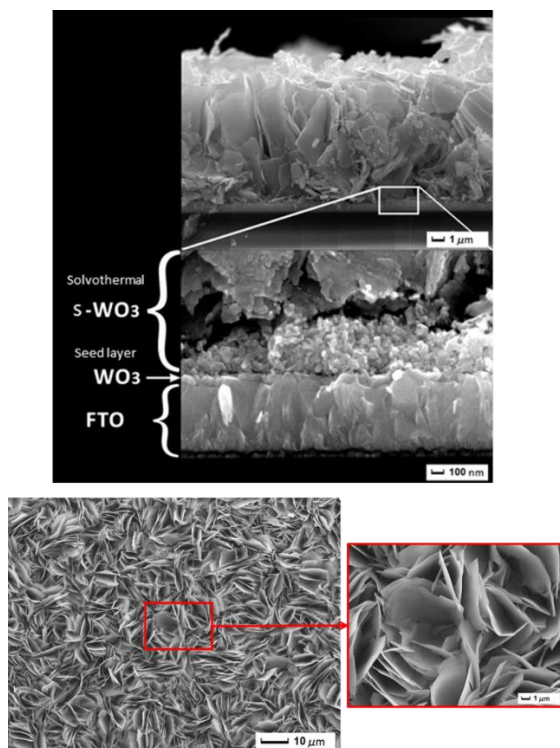


Figure 15.  $\text{WO}_3$  morphology of NF2(Ti)(sl.ds) type sample

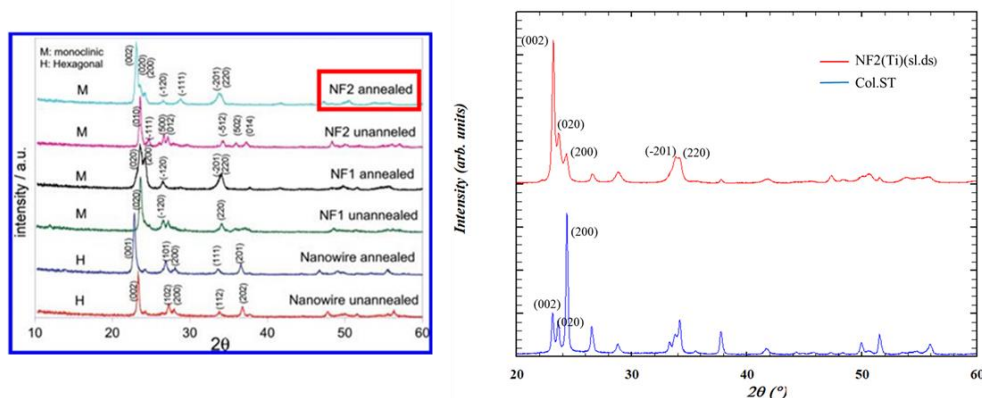


Figure 16 . (A) XRD patterns for solvothermal  $WO_3$  reported by Grimes et al. (Nanoletters, 2011); (B) XRD patterns recorded on NF2(Ti)(sl.ds) compared to the  $WO_3$  standard of known art produced in our laboratory.

One of the most relevant figure of merit for evaluating photocatalytic performance is the quantum yield of charge generation. Inner (APCE) and outer (IPCE) quantum yields of photon to carrier conversion are shown in (Figure 17). IPCE% of NF2(Ti)(sl.ds) and compared a standardized baseline material (col.ST) produced in our laboratory by sol gel-methods. We note that NF2(Ti)(sl.ds) photoconversion is ca. 30% higher than that of col.ST testifying an enhanced photoresponse by the new material. It is also interesting to note that that most of the improvement comes from a better conversion in the visible region, from 400 to 500 nm. Normalization of IPCE% for  $\eta_{e^-/h^+}$ , which is equal to the amount of absorbed photon flux ( $A\%(\lambda)$ ) yields APCE%, which, being higher for the NF2(Ti)(sl.ds) indicate for such material intrinsically higher charge transfer and charge transport efficiencies with respect to our previous standards. The product of such efficiencies peaks at 70% in the near UV, meaning that 70% of the photons absorbed in such regions are converted into useful charge carriers for driving energetically demanding redox reaction, including degradation of organic contaminants. In the blue region of the visible spectrum such efficiency is still significant, with a maximum value of the order of 50%.

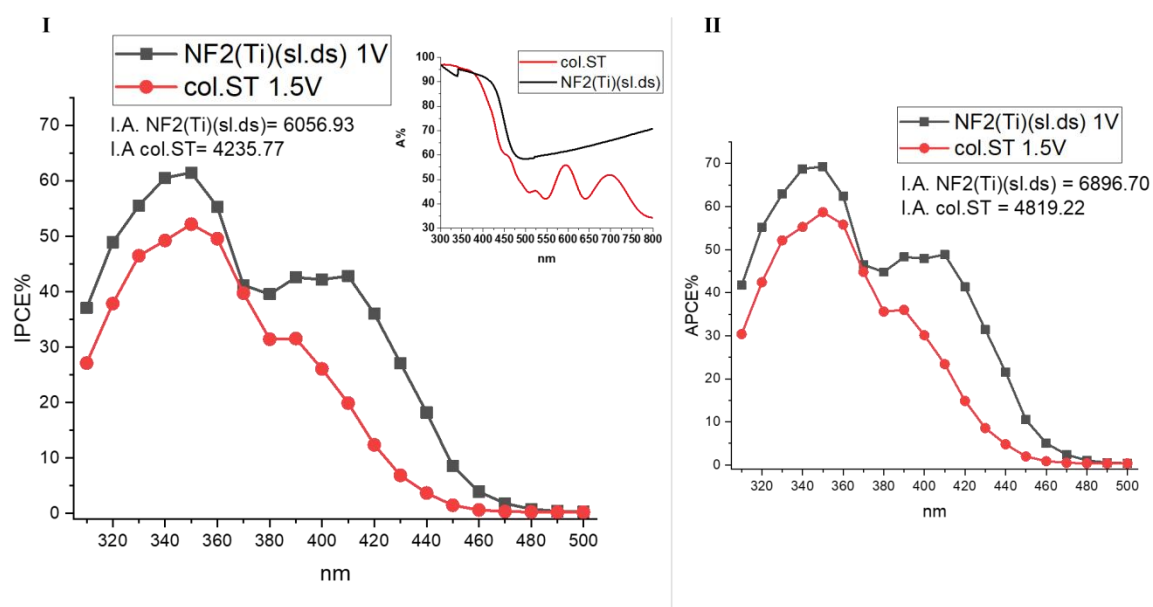


Figure 17: IPCE% and APCE% of NF2(Ti)(sl.ds) and col.ST under, respectively, under 1V and 1.5 V bias, in H<sub>2</sub>SO<sub>4</sub>. Their absorbance spectrum (A= 100-R%-T%) is shown in the inset.

Spherical glass beads, where the yellowish color comes from the presence of a light scattering overcoat of photocatalytic WO<sub>3</sub>, Figure 18 (A) were used to fill a lab scale flow reactor Figure 15(B), where beads filling the glass tubes are illuminated by the 400 nm light generated by a LED strip coiled around the tube, resulting in the production of OH radicals by WO<sub>3</sub>. Water recirculates through the tube until it is photocatalytically decontaminated. We have preliminarily investigated the effect of the photocatalytic treatment on organic matter present in polluted water. The degree of organic contamination is generally expressed by the Chemical Oxygen Demand (COD). The water sample to treat was a real sample collected at the inlet of a waste water treatment plant, with a COD value of 220 mg L<sup>-1</sup>. In Figure 19, the degradation kinetics is reported. It can be observed that the relative COD decreases of about 70% in 1 hour, thus indicating that the photocatalyst is fast and efficient in the decomposition of organic matter.



(A)



(B)

Figure 18. (A) Glass beads conformally coated with lamellar  $\text{WO}_3$  according to the method outlined above; (B) lab scale flow reactor for photocatalytic water treatment.

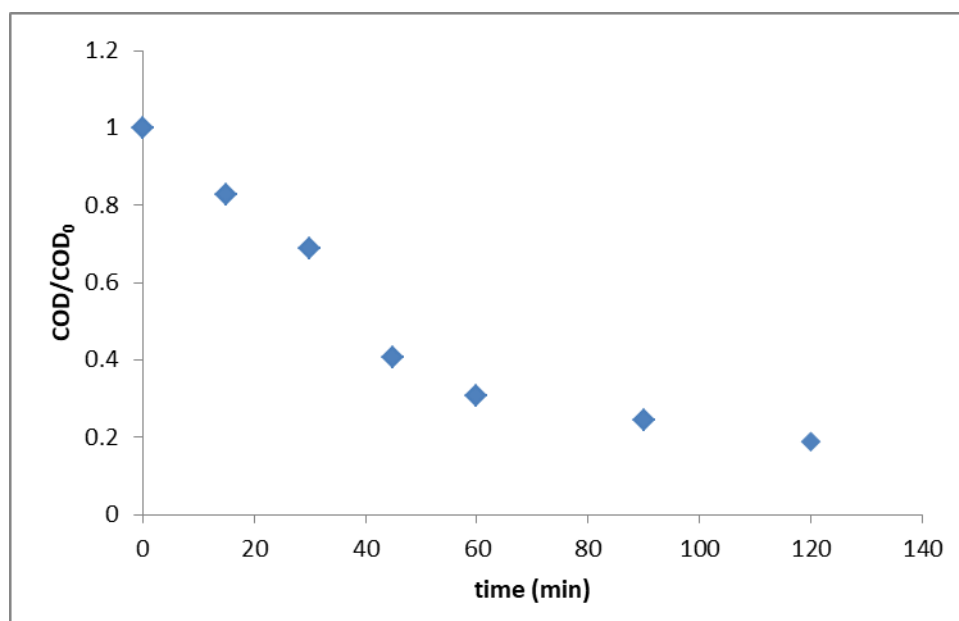


Figure 19: Photocatalytic abatement of the relative COD content of a waste water sample.

### D.4.1.2. Polygon for testing the technological solution for sea pollution cleaning established

Polygon tests were planned in WP4. Due to covid-19 restrictions in travel/movement as reported in PEPSEA COVID 19 Survey, May 2020., the activity has been done in laboratory scale.

In particular, based on the results previously discussed (see D.4.1.1) the activities related to D.4.1.2 were focus on the exploration of adsorbent materials and photocatalysts for contaminants removal from sea water in laboratory scale.

- Testing Toluene removal by using zeolite in salt water.

Adsorption measurements of toluene from solutions at different ionic strength using salt water have been carried out, no significant variations have been observed. Powder diffractions patterns of saturated zeolite from toluene solution are unaffected by the presence of salts and the TOL distribution as well host-guest interactions with the framework are unchanged. (space group  $P 2_1/n$ ).

- Experimental evaluation of CANAM

The properties of CANAM as a remediation agent have been preliminary explored in our labs using diesel fuel and hexane as target compounds, with very promising results. The effect of the salinity and temperature on the adsorption properties have been also evaluated by using a water solution simulating seawater obtained by adding a commercial salts mixture (Instant Ocean® Sea Salt).

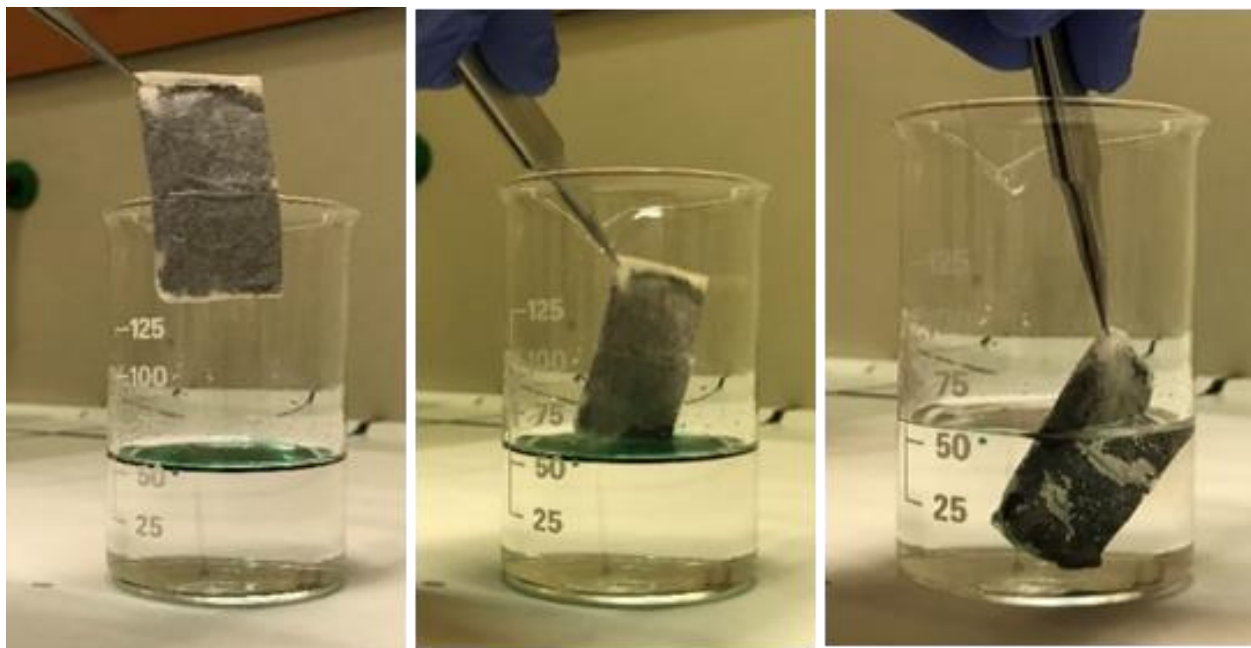


Figure 20: n-hexane adsorption by means of CANAM.

#### n-hexane adsorption

A first test has been conducted using a ca. 50 mg amount of CANAM, enclosed in a cellulose/PE tissue acting as an envelope. The envelope containing CANAM was then immersed in a biphasic solution containing water and n-hexane (which stratifies on water as the top layer, evidenced by coloration with Dithizone, a green hydrophobic dye (Figure 20). After a few seconds CANAM completely adsorbed the hydrocarbon phase, removing the supernatant organic layer from water.

#### Diesel fuel adsorption

This experiment was aimed at the determination of the adsorption capacity of CANAM via gravimetric measurements. Diesel is the main fuel used in small to medium sized motorboats and sailboats (the largest ships mostly use heavier oils) and is therefore ubiquitous hydrocarbon contaminant coastal areas, harbours, and sea areas subjected to intense traffic. The diesel fuel is a mixture of low volatility hydrocarbons which has adverse effects on the marine environment. CANAM, contained in a permeable envelope, was immersed for 1 hour in 18.5 ml of diesel fuel contained in a sealed vial. The CANAM adsorption capacity was 46.60 g/g equivalent to 55.11 litres of fuel per kg of adsorbing agent.

#### Toluene Adsorption



This experiment was performed as previously described in the case of the Diesel fuel adsorption. In this case the average adsorption capacity was 43.10 g of toluene/g CANAM corresponding to 49.71 liters per kg of adsorbing agent.

In addition, the efficiency of photocatalysts composed of a hybrid materials (  $WO_3$  supported on carbonaceous adsorbents and glass spheres) has been tested by determining the degradation kinetics of hydrocarbons (i.e. Toluene) and several emerging contaminants (see Figure 21)

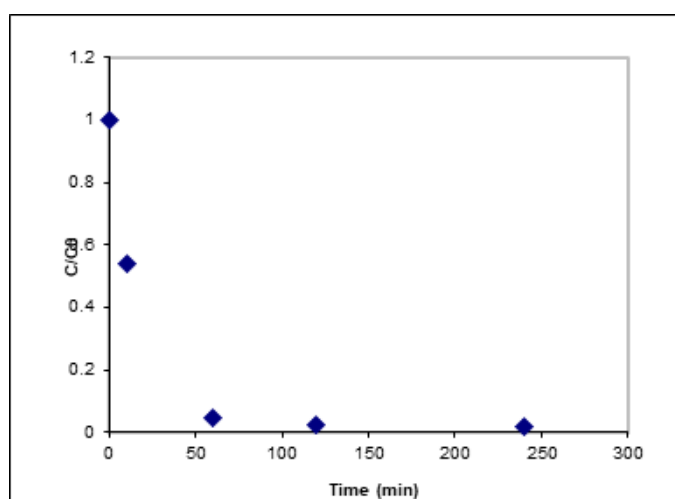


Figure 21: Degradation kinetics of Toluene catalyzed by  $WO_3$  supported on glass spheres

### D.4.1.3. Technological solution for sea pollution cleaning tested

A deep literature survey was reported finalized to the individuation of commercially available materials suitable for water remediation from hydrocarbons contamination.

- **Commercial Adsorbent Materials for Hydrocarbons removal from water**



Water pollution by Diesel fuel (from: <https://www.bsnews.it/2019/04/01/flero-sversamento-gasolio-roggia-scorre-verso-poncarale>).

## Introduction

The aim of this literature survey is the individuation of commercially available materials suitable for water remediation from hydrocarbons contamination. In our specific case, we have considered materials capable of removing, through surface adsorption, significant amounts of hydrocarbon compounds, as those commonly found because of massive spills and water contamination by fuels, oil and its refinery products. We have considered materials of simple use and suitable to their employment in enclosed areas, like bays, harbors, coastal lagoons, freshwater lakes, where a natural confinement of the contaminants occurs, limiting their dilution and simplifying the remediation procedure. It is also important that the remediation materials have an intrinsically negligible impact on the environment and on the water quality itself.



*Figure 1: Example of water pollution by hydrocarbons in an enclosed freshwater area: Como lake nearby Lecco town.*

## Water contamination by Hydrocarbons

Water remediation often requires fast reaction time and an appropriate response in order to limit the damage to the environment caused by pollutants and to reduce collateral effects from the use of the adsorbing agents. At this purpose, some chemical-physical properties of water pollutants should be considered:

- Relative density: the pollutant will tend to sink to the bottom if its density is higher than that of water (salt water has ca. 1.025 g/ml density);
- Vapor pressure: volatile hydrocarbons tend to evaporate;

- Viscosity: this parameter determines the capability of the pollutants of being distributed and dispersed within the water column, or their tendency to emulsify. The larger the viscosity, the lower the pollutant dispersion is.
- Pour point: the temperature below which the hydrocarbon is brought into a semisolid form.<sup>[1]</sup>

As hydrocarbons may present a wide range of these properties, depending on their molecular structure, an appropriate response requires the choice of materials that can be best used in the various situation which are created following the occurrence of water contamination.

### Hydrocarbons Classification

Hydrocarbons may be grouped according to their chemical-physical properties. Based on their density, raw, unrefined oils are subdivided into light, medium or heavy petroleum. Petroleum refinery products, coming from fractional distillation, are then divided based on their boiling point. With increasing of the boiling point, we first find the more volatile fraction comprising gaseous products like butane and propane, then gasoline, diesel fuel, aircraft/lamp fuels, combustion oils, lubricant oils, waxes, bitumen. The ITOPF (International Tanker Owners Pollution Federation) proposes 4 main hydrocarbons groups divided according to their density (Figure 2.<sup>[1]</sup>)

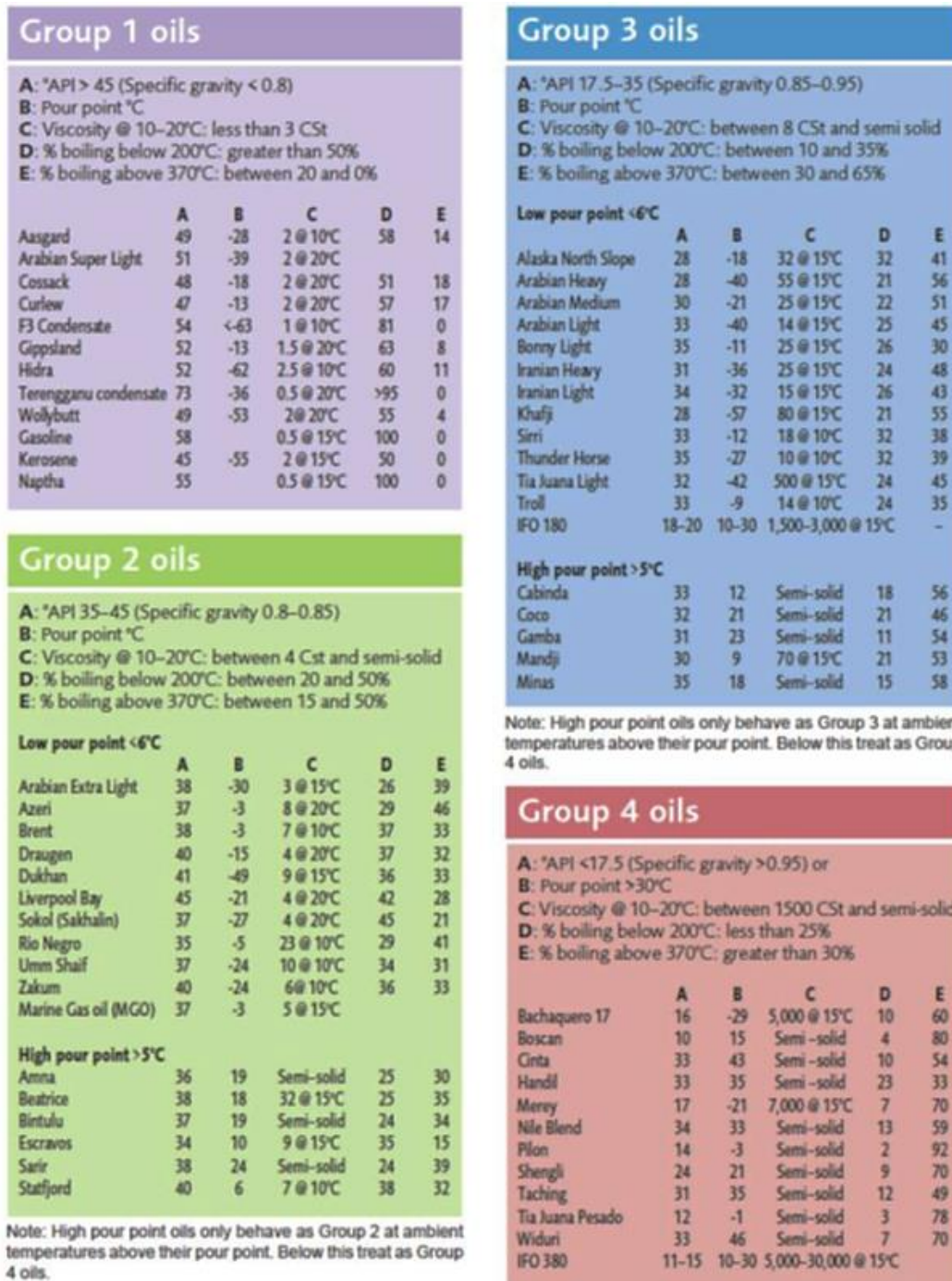


Figure 2: Sub grouping of hydrocarbons according to their density following the ITOPF classification

## Behaviour of hydrocarbons in water basins

Based on their main chemical-physical properties, we can expect different behaviors of hydrocarbons in water. Volatile species will easily evaporate from the water surface at a rate which depends on factors which can accelerate mixing and dispersion, such as wind, water turbulence, sea streams, waves, but also temperature. Normally, components having a boiling point lower than 200°C will pass completely to the atmosphere within relatively short times [1]. Hydrocarbon mixtures having density higher than water (either fresh or sea water) will gradually deposit to the bottom of the water basin, making their removal more difficult. In some other cases, partial solubilization may occur. Owing to these different behaviors, specific remediation actions should be planned and carried out, before environmental damage occurs caused by massive spreading of the pollutants. The use of a material able to adsorb and confine both volatile and soluble substances, even at trace amount, is a clear advantage for an effective environmental remediation intended to mitigate the environmental impact of hydrocarbons contamination.

## Sorbent materials

Sorbents are materials that are used to remove or recover pollutants, which are generally incorporated and confined into the pores of the sorbent agent. The effectiveness of absorbents is therefore a function of their porosity. A variety of organic and inorganic materials have been applied as sorbents for oil spill cleanup. They are also considered one of the most promising solutions in water remediation due to their simplicity and high efficiency.

For a material to be suitable as an oil spill sorbent, it should possess certain physical characteristics which include oleophilicity, hydrophobicity, high uptake and retention capacity. Economic viability is also a desirable property.

Oil spill sorbents can be classified into three categories namely natural organic, natural inorganic, and synthetic sorbents. Natural inorganic adsorbents have been mainly applied to remove dissolved organic contaminants. Indeed, their adsorbing capacities are in the range of 4–20 times their weight in oil with little buoyancy. They include inorganic minerals like alumina, silica, zeolite, clay, alumina-phosphate, and mesoporous adsorbents. Instead, synthetic adsorbents are commercial adsorbents extensively used in severe oil spill cleanup. The most commonly applied synthetic adsorbents are polystyrene, polypropylene, and polyester foams. They have high hydrophobic and oleophilic properties and can sorb up to 70 times their weight in oil. These conventional sorbents used in the process of cleaning oil spills are expensive and usually non-biodegradable. Recently, to improve process sustainability, various agricultural and industrial wastes biopolymers as nonconventional materials that are biodegradable, abundant in nature, low cost, have been considered as part of a novel oil spill remediation process. Nonconventional cellulose- and keratin-based biopolymeric sorbents have been applied in spill cleanup and oil-water separation both in their natural and modified forms.

Sorption is usually driven by the attraction between the outer surface of the sorbents and the oil, and is controlled by van der Waals forces, hydrogen bonding, polarity, steric interactions, hydrophobicity, and other physical and chemical interactions. The sorption processes occur through different mechanisms that often include: a) oil diffuses to the surface of the sorbent; b) capillary action entraps oil in the sorbent pore structure; and c) oil agglomerates in the rough and porous structure of the sorbent.

The oil sorption capacities of different materials are affected by several factors including packing and bulk density of the materials, void volume (porosity), surface morphology, selectivity, and oil retention properties of the biopolymers.

Studies have also shown that the presence of functional groups like hydroxyl, carboxylic, and amino acid groups affect the sorption properties[2].

### Cellulose-based oil sorbents

Cellulose, a major structural material in plant, is a biopolymer. It is usually structured into fibrils with a matrix of lignin and hemicellulose. Cellulosic sorbents are predominantly composed of cellulose, hemicellulose, and lignin. While the lignin contents are hydrophobic, the cellulose and hemicellulose contents are hydrophilic and hence often attract a significant amount of water; however, it remains sparingly insoluble in water and only partly insoluble in organic solvents. The often-low hydrophobicity and buoyancy of natural cellulosic materials is a major limitation for their use in oil-water separations during field applications. Various researchers have made several efforts to increase the hydrophobicity and oleophilicity of cellulose-based biopolymers by physical, chemical, and thermal modifications. It should be considered that the modification processes significantly increase the cost of the final material. Chemical treatment by acetylation is one of the most commonly used modification processes. In this process, the functional groups attached to the cellulose and hemicelluloses are usually replaced by hydrophobic groups through various forms of catalytic and non-catalytic processes. Esterification is also used as a means of increasing the oil sorption and water repellent characteristics of cellulosic biopolymers. Several other chemical modification methods have also been used including acid treatment, surfactant treatment, and the deposition of metal oxides nanoparticles. Thermal treatments have also been used to improve the sorption capacities of cellulosic fibers. In such a case, the final adsorbent is a carbonaceous material. In recent years, a new class of highly interconnected porous and low-density materials with large specific surface areas and porosity has been fabricated using low-cost cellulose biopolymers for applications in oil-water separation. These materials called cellulose aerogels or sponges. Cellulose-based biopolymers and aerogels that have been reported in the literature for oil spill sorption are not commercially available [2].

In order that aerogel-type sorbents derived from nanocellulose precursors can replace traditional oil sorbents in practice, there are several challenges to be addressed in the future:

- 1) the existing hydrophobization process are usually complex and energy-consuming and the process tends to suffer from the drawback of inhomogeneous silylation with a higher Si content on the aerogel surfaces. Thus, one of the concerns is to how to make the process more industrially feasible and effective.
- 2) Many existing recovery methods for oil sorbents, are usually complicated, time consuming, and have high-energy output and low efficiency.

In the following, only commercially available adsorbent materials are reported.

The experimental activities were focused on zeolites (removal of dissolved contaminants) and CANAM (removal of not miscible contaminants).

### CANAM

CANAM (Carbon Nanostructured Advanced Material) is a high-tech material developed and produced by the Swiss company VYRIDIS Ltd (Schwerzistr. 6, CH-8807 Freienbach – Switzerland). Its nanostructured form allows an efficient interaction with a-polar species, like hydrocarbons, which are surface adsorbed and confined in a large amount. CANAM is characterized by quick adsorption kinetics which make it a suitable candidate for water remediation in the presence of high pollutant concentrations. [3][4][5].

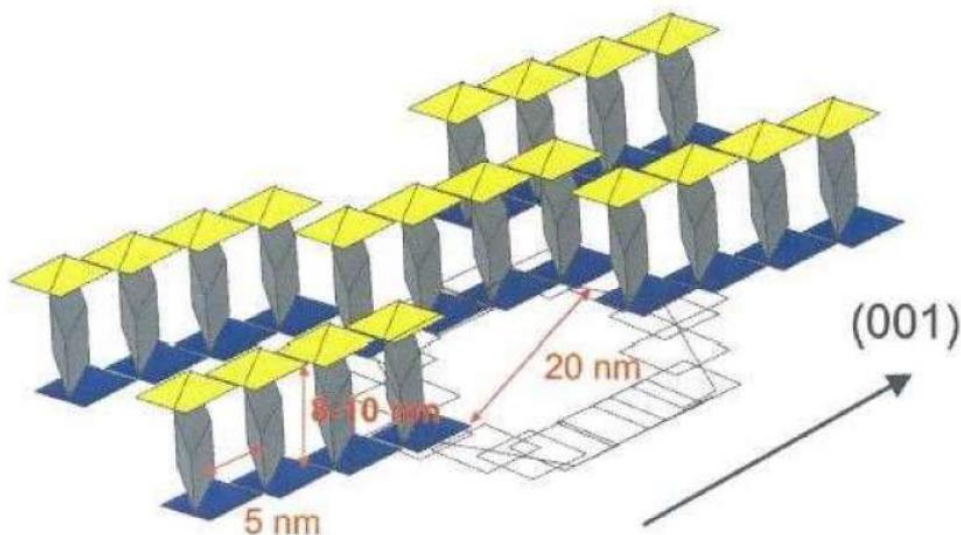




Figure 3: CANAM (CANAM background information, VYRIDIS Ltd).

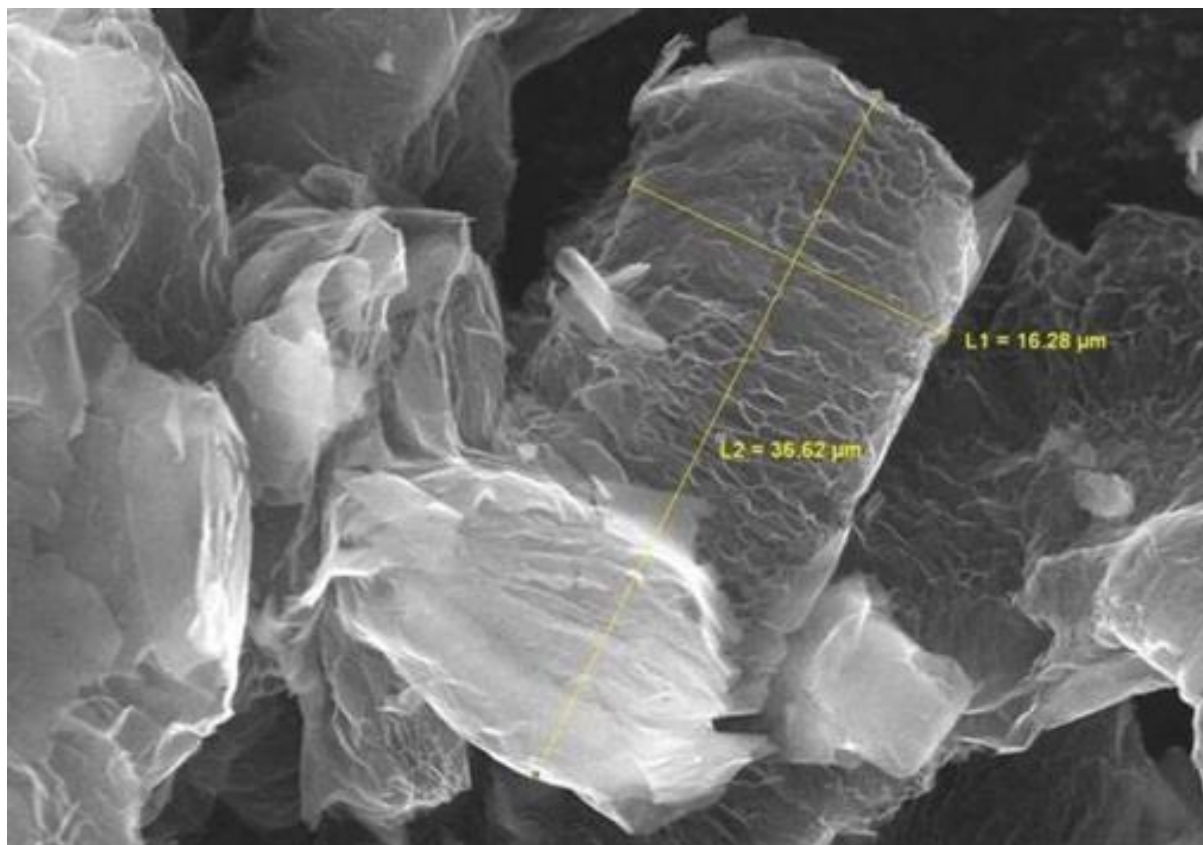
### CANAM Properties

CANAM is a carbon based material, composed mainly by graphite and graphene planes and by tubular structures, whose structural motif is schematized in *Figure 4*. These carbon planes are folded and assembled in the form of a bundle of fibers, tubes, nanoparticles, which generate an extremely porous surface. SEM imaging revealed the simultaneous presence of ultra-micropores (width <1 nm), super-micropores (1-2 nm), mesopores (2-50 nm) and macropores (>50 nm). These different pore size allow to confine non-polar molecules of widely varying dimension, structure and molecular mass. These species are irreversibly incorporated in the carbon network and no subsequent release is observed upon washing, centrifugation or application of a pressure gradient.



*Figura 4: base structure of CANAM (CANAM complimentary information, VYRIDIS Ltd)*

It should be considered that while the porosities are at the nanoscale, the size of the superstructures originated by the assembly of the carbon nanostructures mentioned above generates macro-structures in the 10 e 100  $\mu\text{m}$  size range (Figure5). Thus, CANAM does not pose the safety hazards typical of nanomaterials and is not classified as such. [3][4][5].



*Figura 5: Typical CANAM carbon based superstructures whose size ranges from 10 to 100  $\mu\text{m}$  size (CANAM complementary information, VYRIDIS Ltd).*

CANAM is an inert, non-flammable, hydrophobic material. It is stable below 600 °C, it is benign and compatible with the environment. Traces of either organic solvents or of other possible contaminants introduced during material fabrication are completely absent from its composition.

The average composition of CANAM is as follows:

- 99,760% carbon
- 0,016% chlorine
- 0,023% sulphur
- 0,110% iron
- 0,057% silicon
- 0,022% magnesium

- 0,012% sodium

CANAM shows no detectable amount of heavy metals.

CANAM displays a density range in the order of 0.01-0.001 g/cm<sup>3</sup>.<sup>[3][4][5]</sup>

## Other Commercial Adsorbents

In the market, other high surface adsorbing agents are available. The properties of the following commercial products have been obtained from the products catalogues of the main producers/suppliers of adsorbing materials. Our research was restricted to materials having well defined properties reported in their own accompanying technical sheet and which can be compared with CANAM under the point of view of their adsorption capacity. Thus, all the following materials can be applied to treat significant contamination occurring in enclosed water basins.

### **Denios S.r.l**

Denios S.r.l. is a leader company in the production of materials for supporting chemical processes (Chemical, Pharmaceutical, Oil&Gas, Power, etc.) for those companies which need to treat and manage harmful substances [6] .

### **Adsorbent Agent**

Selected Material: granulated floating DENSORB, oil version, without voc[7]. It is a perlite based material which is also extremely light weight and hydrorepellent. It floats on top of water and is suitable to treat also turbulent waters. It is considered to be excellent to remove heavy oils from the water surface [7]. There are no reported procedures for material regeneration. The declared adsorption capacity is 4.43 l of oil/kg of DENSORB which is typically sold in 7 kg packs.



Figure 7: granulated DENSORB in their floating formulation for oil treatment, without VOC (from: <https://www.denios.it/shop/granulato-densorb-galleggiante-versione-olio-senza-voc-7-kg>).

Tab.1 Technical data sheet for floating DENSORB in granulated form <sup>[7]</sup>.

<b>Composition</b>		<b>perlite</b>	
Adsorption capacity (liters /Kg)		4.43	
Indication of application		Oils, hydrocarbons	
Morphology		granules	
Max (mm)	Granule	size	3
Min. (mm)	granule	size	0.13
Density (g/l)		70	

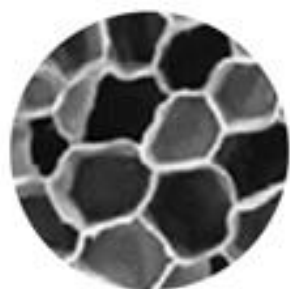
**Amorim Group**

*Amorim Group* is a Portuguese society specialized in cork production and workup. The proposed adsorbing agent is commercially named CorkSorb and is produced by Amorim Cork Insulation <sup>[8][9]</sup>.

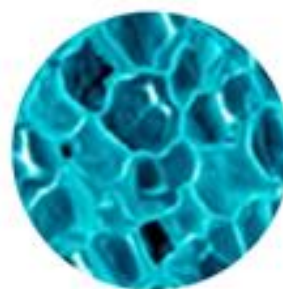
CorkSorb is a natural adsorbent material obtained from the bark of the cork oak (*Quercus suber*)<sup>[10]</sup>, capable to capture diesel oils and a variety of other chemicals <sup>[11]</sup>.

### Adsorbent Agent

Selected Material: the *granular agglomerated CorkSorb for oil* <sup>[12]</sup> is essentially constituted by cork. It is a natural product without environmental issues or associated risks for human health. There is no reported toxicity nor traces of additional chemicals in its composition. This material is suitable for oil adsorption, hydrocarbons, and other chemical substances having hydrophobic properties. These are permanently confined within the Corksorb structure <sup>[13]</sup>. It is a relatively cheap and easy to use material. These combined properties make Corksorb suitable for hydrocarbons removal from water in enclosed areas <sup>[12]</sup>. There are no indications about material regeneration procedures.



Cork cells observed by electronic microscopy



Cork cells after sorbing oil observed by electronic microscopy

*Figure 8: SEM imaging of Cork cells before and after oil adsorption (fonte: <https://www.corksorb.com/en/corksorb/>).*

Technical data sheet for granulated CorkSorb <sup>[13]</sup>:

<b>Composition</b>	<b>100% cork</b>
Adsorption capacity	4.8 l/kg
Indication of Application	Oil, hydrocarbons, non polar substances
Size (mm)	420x420x790
Density (g/l)	102

The material comes under various packing solutions (pillows, bags, socks, booms). The typical weight of a bag is 7.65 Kg <sup>[13]</sup>.

***Airbank S.r.l.***

AIRBANK is a leading company for industrial safety and environmental remediation. It offers a wide variety of HSE products (Health Safety Environment) <sup>[14]</sup>.

**Adsorbent Agent**

Selected Material: OKO-PUR is a recycled material based on polyurethane, obtained from the insulating section of refrigerators. It is sold as powder or as floating hydrophobic granules. It is reported to capture up to 95% of hydrocarbon spills from the water surface on which it floats easily, even when saturated. AIRBANK declares that OKO-PUR is the most used material for environmental remediation. Procedures for material regeneration are not reported <sup>[14]</sup>.



Figure 9: left, granulated OKO-PUR; middle powdered OKO-PUR; right OKO-PUR during an adsorption test from the water surface. (source : <https://www.airbank.it/it/p/1/assorbente-legante-in-polvere-e-granuli-a-saturazione-totale>).

OKO-PUR technical sheets<sup>15]</sup>:

Chemical Composition	Recycled Polyurethane
Adsorption capacity	4.4-11.8 l/kg
Application	Oils
Morphology	Powder or granules
Density (g/l)	Not Available

OKO-PUR is typically sold in 6.8 Kg bags

Test1 S.r.l.

*Test1* performs scientific research, technology development and experimentation of innovative products for oil disasters. It holds an international patent for an oil absorbent product, unique worldwide, for preventing and reclaiming environmental damage caused by oil spills. Test1's mission is to reduce companies' environmental impact, while reducing the cost impact of the environment protection on companies. Test1's administrative HQ are located in Brescia, with a research laboratory and pilot production facility and representative office in Edinburgh<sup>[16]</sup>.

## Adsorbing Agent

Selected Material: FoamFlex200 is an innovative, patented oil absorbent technology for hydrocarbons and their derivatives. The product is an open-cell oleophilic polyurethane foam with a hydrophobic effect greater than 95%. This allows the intact recovery of spilled hydrocarbons with less than 5% water. <sup>[16]</sup>

Foam Flex 200 technical sheets <sup>[15]</sup>:

Chemical Composition	Polyurethane
Adsorption capacity	≈ 30 l/kg
Application	hydrocarbon
Morphology	Not Available
Density (g/l)	Not Available

It can absorb about 30 times its own weight of any hydrocarbon. Using a wringing process, FoamFlex200 can be reused over 200 times. One kilogram (1 kg) FoamFlex200 can absorb about 6 tons of hydrocarbons <sup>[16]</sup>.



## Conclusions

The adsorbent performances of the materials considered in this report are summarized in *Table 4*.

Table 4. Adsorption capacity

Materiale	Adsorption capacity (l/kg)				
<i>Granulated DENSORB</i> Denios S.r.l.	4.43				
<i>CorkSorb</i>	4.80				
Amorim Group					
<i>OKO-PUR</i>	4.4-11.8				
Airbank S.r.l.					
<i>FoamFlex 200</i>	30				
Test1 Srl					
<i>CANAM - Diesel</i>	55.11				
VYRIDIS Ltd					
<i>CANAM - toluene</i>	49.71				
VYRIDIS Ltd					
Pad Sentec™	Meltblown 99.7%	polypropylene Blue pigment 0.3%	150-200 (depending on the pollutant)	L/1 on	pad the
Barrier Sentec™	Meltblown 90%	polypropylene Other no harmful fibers 10%	30-40 (depending on the pollutant)	L/1 on	barrier the

Our comparative analysis points out the large adsorption capacity of CANAM, tested on both toluene and Diesel oil, which exceeds by a factor of ca. 10 the known performance of other commercial materials. Consideration based on cost/performance analysis, together with specific environmental needs found in

an enclosed part of the sea may guide an informed choice about the best material to adopt. In general, no regeneration procedures are reported for any of these adsorbing agents, which can be at best considered as easily disposable after having captured the target pollutants.

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## Annex 1

Removal of oil and / or oil mixture in marine environment is usually performed as follow [1]:

- removal of pollution sources,
- prevention of spread of oil and / or oil mixture,
- collection of spilled oil and / or oil mixture,
- chemical treatment (use of dispersants) of spilled oil and / or oil mixture as required,
- removal of seawater pollution,
- disposal of collected hazardous waste.

The use of dispersants is not permitted in protected areas of nature listed in Annex V, point 1 of the Intervention Plan [1].

For the removal of pollutants, sorbent materials are often employed. Sorbents are insoluble materials or mixtures of materials used to soak up liquids through the mechanism of absorption, adsorption or both. Absorbents allow oil to penetrate into pore spaces in the material they are made of, while adsorbents attract oil to their surfaces but do not allow it to penetrate into the material.

There are several materials that can be successfully employed, and Member States are encouraged to ensure cost-effectiveness in achieving environmental benefits [2]. Protecting marine environments from chemical pollution is an issue (art. 31 of [3]) of the Environmental Protection Act. In order to satisfy regulatory indications on the need of adsorbents of natural origin such as natural zeolites and environmentally friendly such as those made of plant fibers. The latter are therefore acceptable for decontamination of protected marine environments[4-6].

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