Kill•Spill

Integrated Biotechnological Solutions for Combating Marine Oil Spills

Deliverable D5.5

Report of factors affecting the performance of sequestering sorbents

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1   About this deliverable

In this deliverable will be discussed factors affecting sorption of crude oil on different sorbents. This will be illustrated by experimental data with toluene and with crude oil.

2   Introduction

The threat of oil spills increases with the increasing demand of world industry on crude oil production. Big oil spills occurred during the last decades because of crude oil transportation or gas and oil production by drilling from the seabed. It is estimated that worldwide , 224,000 tons of crude oil polluted the marine environment due to oil tanker spill between 2000 and 2011 (Wahi et al. 2013). When oil spill occurs, the treatment of oily contaminated water is a critical issue for the environmental protection. Spilled crude oil can be effectively removed by advanced technologies, but these treatments are usually expensive, request special equipment and combat against oil spill is difficult under bad weather conditions. Usage of sequestering sorbents could be a promising choice of treatment because of its simplicity, effectiveness, and feasibility when appropriate sorbent is used.

An extensive experimental activity was carried out on the characterization of selected active capping materials for oil spill contaminated sediments. Capping is a conventional sediment remediation strategy and it is aimed to reduce the contaminants release to the pure water. Capping consists in a clean material layer above the contaminated sediment, operating a barrier to the contaminants transport. Sand or clean sediment are common used as passive capping materials to reduce the contaminants migration to the overlaying water (Lampert et al. 2011). The use of sorbent materials (active capping) is certainly more effective for contaminants transport limitation (Reible et al. 2006) (Cornelissen et al. 2012) combining the effect of diffusive and sorptive barrier. In the perspective of the contaminated sediment remediation sorbent materials for active capping application are very promising for the hydrophobic organic compounds (HOCs) removal. In order to test and compare the sorbent material performances toluene was adopted as target dissolved contaminant. Tested materials were characterized in aqueous phase in order to screen their property; furthermore the effect of the sea water composition on the adsorption phenomena was investigated. Materials characterization was carried out both by kinetics and equilibrium (isotherms) batch tests.

3   Mechanism of oil removal by adsorption

Adsorption is the attraction between the outer surface of a sorbent and a sorbate (crude oil). Molecules of crude oil accumulate on the sorbent surface without penetrating into the sorbent. In general, oil adsorption occurs in three steps: diffusion of crude oil molecules to the sorbent surface, entrapment of crude oil into the sorbent structure by capillary action, and finally agglomeration of oil droplets in porous and rough structures of the sorbent (Wahi et al. 2013). It is also necessary to take in account that adsorption reaction should be considered completely reversible. After equilibrium time there is dynamic balance between adsorption and desorption processes (Limousin et al. 2007).

In oil adsorption various types of attractive forces act together. The attractive forces can be grouped into the chemical (covalent or hydrogen bonds), electrostatic (ion–ion, ion–dipole), and physical (dispersion energy, energy of molecules movement) forces. Adsorption could be spans between monolayer crude oil adsorption on homogenous surface of sorbent and multilayer crude oil adsorption on heterogeneous surface of sorbent. Because crude oil is a multicomponent a multicomponent solute the prediction of adsorption behaviour is difficult (Wahi et al. 2013).

Crude oil and sorbent can form aggregates of three distinct types: droplets, solid, and flake aggregates. Droplet aggregates are the most common type, which are defined as individual micro-

sized oil droplets surrounded by solid particles, and sometimes more than one droplet is present to from multi-droplet aggregate (scale of a few μm). Solid aggregates are a mixture of oil and solid bodies of various shapes (scale of tens μm). Flake aggregates are thin sheets, in which solid and oil particles are arranged in an ordered configuration (scale of up to mm) (Le Floch et al. 2002).

4   Properties of sorbents affecting sorption effectiveness

Sorbent materials can be classified into organic, inorganic and synthetic organic products. Organic sorbents include straw, corn cob, wood fiber, sawdust, cotton fiber, kapok fiber, wool fiber, kenaf fiber, rice husk, coconut husk, cattail fiber and bagasse. Mineral inorganic products include perlite, graphite, vermiculite, zeolites, bentonites, clay, fly ash, sand, zeolites, kaolin, quartz, montmorillonite, calcite and diatomite.

4.1   Hydrophobicity

The hydrophobicity of the sorbent determines its wettability by oil or water. Oil attraction by sorbent could be caused by hydrophobic interaction between sorbent and oil. In addition hydrophobic sorbents has low water uptake and are thus protected from collapse of their microstructure due to high water uptake. The hydrophobicity of organic sorbents, derived from plants, is closely connected with their wax content which also influences the buoyancy of the sorbent (Likon et al. 2013).

4.2   Functional groups on sorbent surface

Oil adsorption is closely related to functional groups on the sorbent's surface. Functional groups conductive for oil adsorption are alcohol groups, phenolic group, carboxylic group (Said et al. 2009), the asymmetric and symmetric aliphatic CH_2 and CH_3 stretching associated to n-alkanes, fatty acids, aldehydes, ketones and n-alkyl esters (Wahi et al. 2013).

4.3   Surface morphology

Another important characteristic is the surface morphology of the sorbent. Many excellent natural organic sorbents like kapok fiber or populous seed contain microtubular structures, hollow lumen, twists or crimps, which together with surface roughness and porosity enlarge the surface area available for adsorption and also enable maximum oil entrapment into their empty structures (Abdullah et al. 2010, Wahi et al. 2013). These structures can also be used for microbial immobilization. Inorganic sorbents can have porous a structure, which increases the surface area and the number of places suitable for oil sorption.

4.4   Surface area and particle size

Surface area is closely related to particle size and surface morphology. High oil removal is observed for sorbent having small particle size. In fact, small particles have high available surface area and correspondingly a high number of oil binding sites and therefore possess high adsorption potential. After adsorption equilibrium, oil removal efficiency is independent of particle size due to coating of sorbent active surface. In fact, oil adsorption is mainly determined by the surface morphology and by the hydrophobicity of the sorbent (Angelova et al. 2011).

4.5   Pore size

Increase in sorbent pore size decreases oil adsorption efficiency, and reduced pore size allows complete oil droplets capture (Bansal et al. 2011). Next to this, low internal pore diameter permits

high oil adsorption. The same applies to entangled structures whose presence increase sorption capacity despite the occurrence of wide pores (Abdullah et al. 2010).

4.6   Surface interaction

Surface interactions, namely the surface tension and surface energy, determine the sorption capacity of a sorbent. From this point of view sorption capacity differs among different sorbents and types of oil, due to difference in oil surface tension and sorbent surface energy. Sorbent with low surface energy has higher wetting capability by oil than water (Wahi et al. 2013).

The stabilization energy it the energy of attachment of particles adsorbed at the interface between water and oil. This energy is impacted by the type of emulsion, water-in-oil or oil-in-water, which establishes position of the particles relative to the oil–water interface (Binks and Lumsdon 2000). The best stabilization effect occurs when the particles are partially wetted by both, the water and oil phase. In addition, the hydrophobicity, functional groups on sorbent surface, size, and shape of the particles can impact the stability. Next to this, the presence of solvents, surfactants and/or oil dispersants can alter the interfacial tension and surface wettability, and thus, can alter the stabilization energy. Hence hydrophobic particles, which tend to be oil-wetted, prefer water-in-oil emulsions. On the contrary hydrophilic particle, whichs are water-wetted preferentially stabilize oil-in-water emulsions. Extremely hydrophilic or hydrophobic particles are nearly completely wetted by water or oil, respectively and prevent the formation of stable emulsions (Aveyard et al. 2003).

4.7   Buoyancy

Buoyancy reflects the ability of aggregates consisting of oil and sorbent to stay afloat on water surface and thus influences the oil adsorption performance. Buoyancy of sorbent is given by its hydrophobicity which can be influenced by wax content in organic sorbents, derived from plants (Khan et al. 2004). In addition, the presence of long and branched hydrocarbon chains on the surface of sorbents is identified as a contributing factor to buoyancy and hydrophobicity (Likon et al. 2013). Many natural organic sorbents have poor buoyancy because they have big water sorption capacity and tend to sink in the aquatic environment (Angelova et al. 2011).

5   Crude oil characteristics

Once oil is released into the marine environment, it undergoes complex physical, chemical and biological transformations, including spreading, drifting, dispersion, stranding, and weathering. Properties of crude oil like type, wettability, amount of water-soluble fractions influence the fate and distribution of oil in water column. Crude oil in water can be present in different forms, namely as dispersed oil droplets in water column, dissolved oil components, emulsions or as a free oil fraction forming floating layer on the water surface. Free oil fraction can be easily removed from water by skimming. In contrast, dispersed oil droplets and oil emulsions are more difficult to treat due to their high stability in the aqueous phase.

5.1   Viscosity

Viscosity of crude oil is one of the parameters influencing interactions with sorbents. Oils having high viscosity are difficult to disperse, and less likely to form aggregates with solids, while low viscosity oils are more prone to form aggregates (Le Floch et al. 2002). Viscosity of oil also influences buoyancy of aggregates formed. Aggregates from highly viscous crude oils settle faster than with less-viscous oils. This could be explained by the density because aggregates formed from more viscous oil have higher density than those from less-viscous oil (Omotoso et al. 2002).

5.2 Droplet size

When oil droplets are formed and dispersed in water, they tend to coalesce to minimize the system energy. However, small colloidal particles situated at the oil–water interface are able to prevent the coalescence of oil droplets (Aveyard et al. 2003). From a thermodynamic point of view, a large number of small oil droplets is more favorably driven to the sorbent than a small number of larger droplets because the greater number of oil droplets results in a higher collision frequency and thus a greater number of aggregates (Gong et al. 2014). Small droplets can infiltrate into the micropores of sorbent where large droplets would not fit and small droplets have also larger surface areas and undergo higher rates of biodegradation due to enhanced oil availability (Wahi et al. 2013).

5.3 Composition

Crude oil is mixture of components, of which composition widely varies. Composition depends on its geographic origin and processes that led to crude oil formation. Main components are resins (4-25%), saturates (25-83%), aromatics (13-43%) and asphaltenes (0-12%) (Aske et al. 2001). Polar hydrocarbons are needed for aggregates formation since polar compounds in oil droplets enhance the adhesion between oil droplets and polar (hydrophilic) sorbent particles. Asphaltenes and resins are amphiphilic components in crude oil. The polarity of crude oil increases with increasing concentrations of resins and asphaltenes (Quintero et al. 2009).

5.4 Density

With increasing density of the oil a decrease penetration into the layer of sorbent is observed. In case of heavy oils, high rate of sorption is observed during the first 10-15 minutes of contact. After this period the sorption rate is decreasing until adsorption–desorption equilibrium is reached. The observed sorption equilibrium in the case of light oil products is achieved faster than with heavy oil. With respect to the influence of the density of the oil product on the sorption kinetics it has been found out that the higher the density of the product the lower is its depth of penetration into the layer of adsorbent (Angelova et al. 2011).

6   Outer Factors affecting performance

Since sorption is determined by its equilibrium, it is largely influenced by pH, the concentration of ions (salinity) and the interactions between different substances present in crude oil and water. Another important factor is type of interactions occurring between the sorbent and the sorbate. In other words whether sorption is mainly governed by chemical or physical processes and whether it is a monolayer or multilayer sorption process.

6.1   pH

Changes in pH affect surface properties and binding sites of sorbent, emulsion breaking/size of oil droplets and surface charge of oil droplets. It is not surprising that different sorbent behave differently towards change of pH. With chitosan crude oil removal efficiency increases in acidic and basic conditions in comparison with removal in neutral conditions (Ahmad et al. 2005). This could be explained by ionization of crude oil or sorbent groups or by hydrolysis of crude oil. Heavy oils containing mainly alkanes are less affected by pH. This is due to their chemical stability and absence of ionisable or hydrophilic groups, which could be influenced by pH (Simonovič et al. 2009) .

6.2   Temperature

Brownian motion is dependent on temperature and the speed of Brownian motion increases with increasing temperature. The number of interactions between oil and sorbent, increases together with the speed of molecules motion. At low temperature the Brownian motion will be slow and adsorption of oil will be reduced. At high temperature (more than 80°C) adsorption of oil will also be reduced. At high temperature the speed of motion increases, thus more energy is required for adhesion of the oil molecule onto the sorbent surface. In addition, the randomness of oil adsorption–desorption increases, which lessens the probability of oil attachment to sorbent surface. Besides, increase in oil temperature causes decrease in oil viscosity, increase in oil solubility in water, and increase in oil drainage from sorbent surface (Wahi et al. 2013).

6.3   Salinity or ionic strength

Salinity and ionic strength affect the flocculation of mineral particles and modify surface properties of oil droplets. Formation of aggregates with minerals is inhibited in fresh water (salinity of 0–1; the numbers of the dimensionless salinity scale represent grams of dissolved solids in one liter of water) as compared to salt water (salinity above 10) (Le Floch et al. 2002). The sufficient salinity is prerequisite for interaction of crude oil with mineral sorbent. The sufficient value of salinity depends on both the crude oil type and the nature of sorbent used (type of minerals). Below this value there is a linear decrease of aggregate formation. On the contrary high salinity seems to have negligible effect on aggregate formation. The mechanism by which salinity affects the formation of aggregates is by the control of the electrical double layer thickness of oil and mineral particles (Schramm 1992). As the salinity increases, the electrical double layers on particles surfaces are compressed, which decreases the repulsion potential of particle surfaces and facilitates attractions between the particles. However, once the double-layer thickness is below a certain threshold value, further increase in salinity has less influence on aggregates formation (Le Floch et al. 2002, Gong et al. 2014).

6.4   Pressure

Approximately 10 m of water depth produces a pressure of 1 atm. Oil plumes in deep sea are formed during many oil spills due to the release of oil/gas mixture from sea floor. Under this conditions especially high pressure (higher than 16MPa) and low temperature (-1 to 4°C) the crude oil behaves differently. Methane may be converted to gas hydrates, hydrocarbons above C14 can also form a waxy solid phase (Le Gall et al. 2014). Gas, gas hydrates, waxy hydrocarbon solid, sediment, oil, and even more phases co-exist in deep water plumes. However, detailed information on oil interactions under deep-sea conditions is still lacking, although effects of temperature on adsorption of hydrocarbons have been well documented for oil spills in deep sea (Gong et al. 2014).

6.5   Hydrodynamic conditions

Wave energy is an important factor for natural removal and cleaning of stranded oil. High energy causes significant sediment motion and flushing of interstitial water in beach sediments and coastal marshes. These combined processes abrade oil from sediment grains and disperse it in the water column (Lee et al. 2003). In open sea, wave energy in combination with mixing energy breaks the oil into small droplets and enhance collision between oil droplets and sorbent particles which accelerate sorption (Sun et al. 2010).

6.6   Presence of other substances (dispersants)

Application of oil dispersants is a possible marine oil spill response. Generally, oil dispersants are complex mixtures containing three types of chemicals: solvents, additives and surfactants. Solvents

are added primarily to promote the dissolution of surfactants and they reduce the dispersant's viscosity and affect its solubility in spilled oil. Additives may improve the dissolution of the surfactants into an oil slick and increase the long-term stability of the dispersant. Commercial dispersants of chemical nature usually consist of two or more surfactants. These surfactants added in fixed ratios can emulsify oil, and hydrocarbon-based solvents can help in breaking up large clumps of high molecular weight occurring in viscous oil. Oil dispersants lower the oil–water interfacial tension, thereby breaking oil slicks into fine droplets. They accelerate oil dispersion into the water column and dissolution of the hydrophobic oil components (Gong et al. 2014).

Because of their amphiphilic nature, dispersants/surfactants can exert two contrasting effects on adsorption. On the one hand, surfactants can increase the apparent solubility of oil, by entrapment of non-polar substances from crude oil in the hydrophobic cores of surfactant micelles, thereby reducing sorption and promoting desorption. On the other hand, the dispersant/surfactant itself is subject to sorption. The sorbed dispersant can provide additional sorption capacity for oil. The effects of surfactants on oil sorption and desorption depend on the relative importance of these two contrasting effects (Zhang and He 2011).

7   Experimental characterization of selected sequestering sorbents

Activities of UNIRM partner consisted in the characterization of the performance of selected sequestering sorbents potentially applicable in the hydrophobic organic contaminant removal from sea sediment impacted by hydrocarbon spill. These materials were tested in the perspective of their potential use as active materials for *in situ* capping of contaminated sediments. The tested materials are listed in Table 1   .

Table 1   Sorbent materials used in test with toluene

No.	Sorbent	Size, Specification	Supplier / provided by
1.	Commercial clinoptylolite	1-2 mm	Rota, Turkey
2.	Graphite	0.5-1 mm	EC-100 Sales Inc
3.	Activated carbon (AC)	1.680-0.841 mm; surface area 600 m^2/g	Sigma Aldrich
4.	Granular AC	>2.380 mm= 5%, < 0.595 mm = 5%; Surface area 1050-1150 m^2/g	Carbone Italia
5.	Organophilic clay PM-199 (OC)	1 mm (1% max), 0.425 mm (70% min), 0.3 mm (25%max), 0.15 mm (3% max), pan (1% max).	Cetco Poland sp. z o.,
6.	Peat moss (PM) and Biochar (BC)	powder materials	provided by partner ICTP
7.	single-walled CNTs (SWCNTs), multi-walled CNTs (MWCNTs) and functionalized CNTs	powder materials	CheapTubes
8.	Zero valent iron (ZVI)	1-2 mm	Iron Aggregate ETI CC-1004 Connelly-GPM Inc.

Toluene was chosen as target dissolved contaminant in order to compare the adsorption behavior of the different materials. Batch tests were carried out to investigate adsorption kinetics and to obtain

experimental isotherms for all the materials. All the tests were initially carried out in deionized water and then the ionic strength was increased by using Sigma Aldrich Sea Salt to simulate the behavior in the real conditions. The ionic strength (I) of the single test was assumed to be zero in deionized water and 0.7 M in synthetic sea water; the pH of both solutions was 7 and the temperature was kept at 25°C for all the tests. The range of the investigated toluene concentration was between 0 and 400 mg/L.

For the <u>kinetic tests</u> 20 mg of selected sorbent was mixed with 20 mL of toluene target solution (ratio $W_{solution}:W_{material}=1:1$). This ratio was used for all the materials except for the single-walled carbonanotubes (SWCNTs; 1.5 mg in 10 mL, $W_{solution}:W_{material}=1:0.15$). The sorbents were mixed with the solution for different reaction time, namely 0.25, 0.5, 1, 2, 3, 4, 5, 6, 7 and 24 hours; all tests were stirred using a rotary shaker (15 RPM). An aliquot of the solution was sampled and analyzed before and after addition of the sorbent materials. C_o is the toluene starting concentration and $C_{(t)}$ is the toluene concentration after incubation time t.

For the <u>equilibrium tests (adsorption isotherms)</u> different solutions were prepared, 20 mL (10 mL for SWCNTs), at different toluene initial concentrations; 20 mg of sorbent (1.5 mg for SWCNTs) was added to these solutions. All the tests were maintained under mechanical stirring on a rotary shaker (15 RPM). C_0 was experimentally determined for all the tests and C_{eq} was measured after 24 h; the adsorbed amount was calculated as:

$$S_{eq}=(C_0-C_{eq})*V_{solution}/g_{sorbent\ material}$$

where C_0 and C_{eq} are the toluene initial and equilibrium (after 24h) concentration in mg/L, $V_{solution}$ is the mL of the spiked solution and S_{eq} is the mg of sorbed toluene/g of sorbent material.

Toluene concentration was determined by gas chromatography (DANI GC 1000 equipped with a DANI 86.50 headspace auto sampler, Milan, IT) using a capillary column (75 m length, 0.53 mm ID, TRB 624) and a flame ionization detector (FID). For headspace analysis, a 100 μL sample was diluted with 3 mL of deionized water and sealed in a 10 mL headspace vial fitted with a Teflon-faced butyl septum.

The oven program temperature was: 60°C for 0.5 min increasing at 6°C/min to 110°C for 0 min, then increasing at 15°C/min to 180°C for 0 min. Head space sampler conditions were: oven temperature 70°C, manifold temperature 75°C, transfer line temperature 180°C, soft shaking.

7.1   Kinetics tests with toluene

The experiments have clearly shown that some of the selected materials do not exhibit a significant adsorption capacity for toluene. Clinoptylolite, graphite, functionalized CNTs, zero valent iron (ZVI) and peat moss only adsorbed less than 10% of the toluene in both deionized and synthetic sea water (results not shown). Although these materials do not have a relevant adsorption capacity, they are still under experimental investigation due to their potential use for other contaminants removal such as heavy metals or hydrophilic compounds occurring in oil.

The other tested materials (ACs, OC, BC, MWCNTs and SWCNTs) have shown a significant toluene adsorption and 4 hours, on average, were necessary to reach the equilibrium condition. Toluene dissolved concentration as function of time is shown in the following graphs (Figure 1 to Figure 6) for the single tested materials and in synthetic and sea water solution.
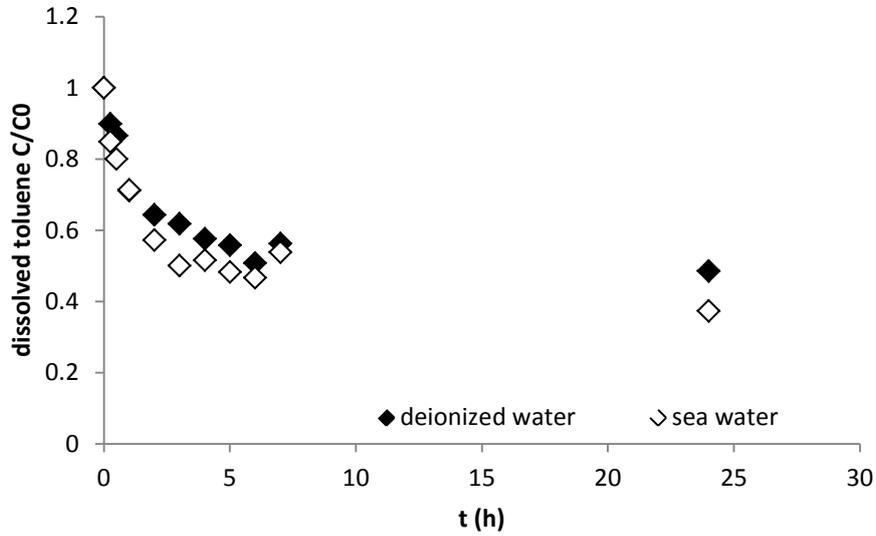
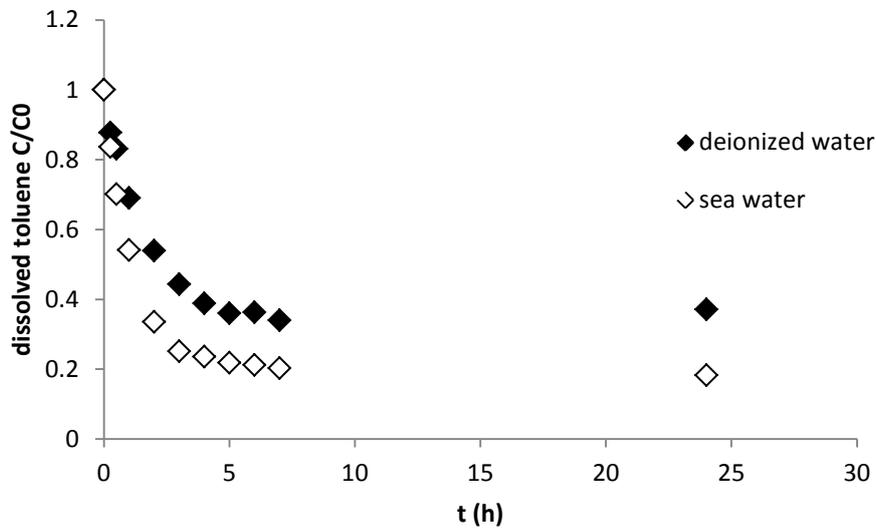**Figure 1** **Kinetic tests with dissolved toluene in deionized and synthetic sea water onto activated carbon (Sigma Aldrich)**

Figure 2 **Kinetic tests with dissolved toluene in deionized and synthetic sea water onto activated carbon (Carbone Italia)**
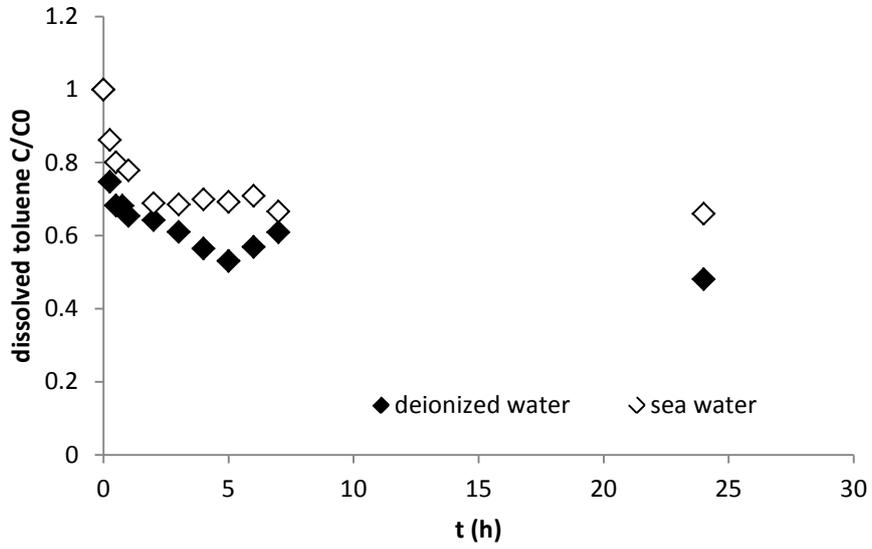
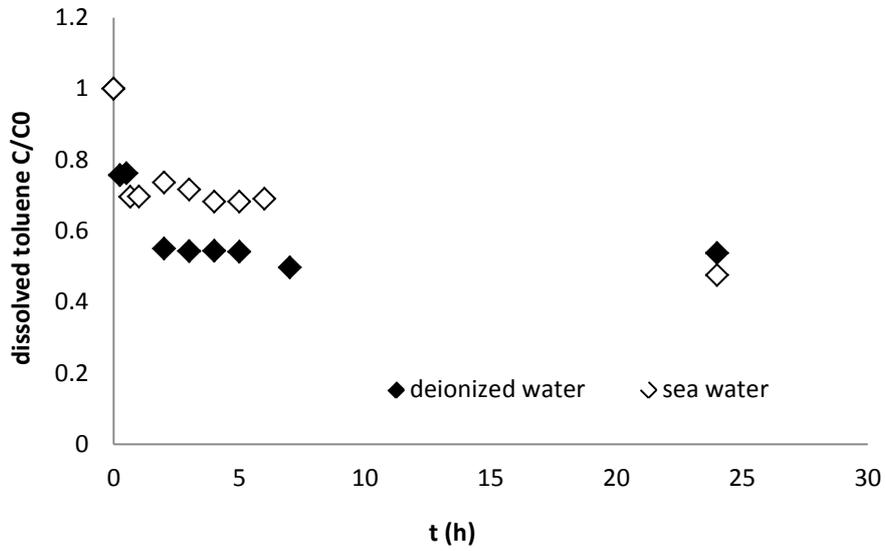**Figure 3**   **Kinetic tests with dissolved toluene in deionized and synthetic sea water onto organophilic clays**

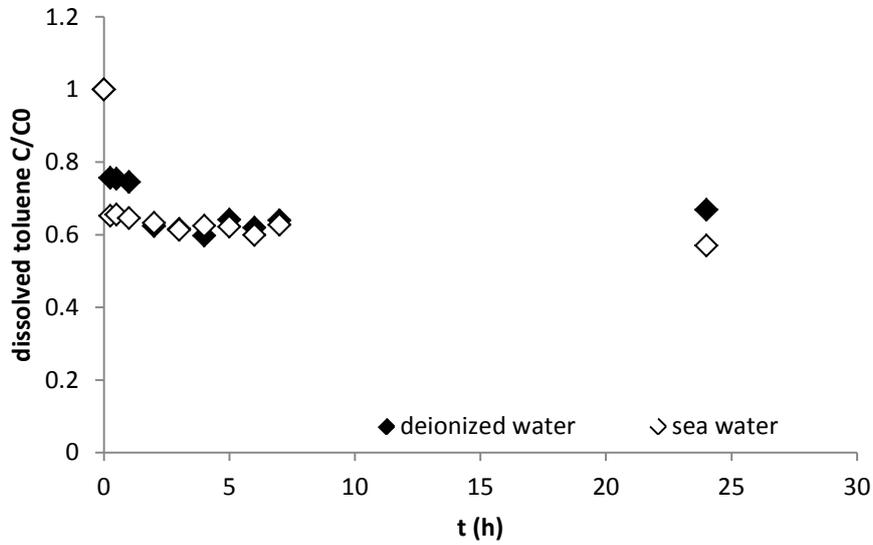**Figure 4**   **Kinetic tests with dissolved toluene in deionized and synthetic sea water onto biochar**

Figure 5   **Kinetic tests with dissolved toluene in deionized and synthetic sea water onto multi-walled carbon nanotubes**
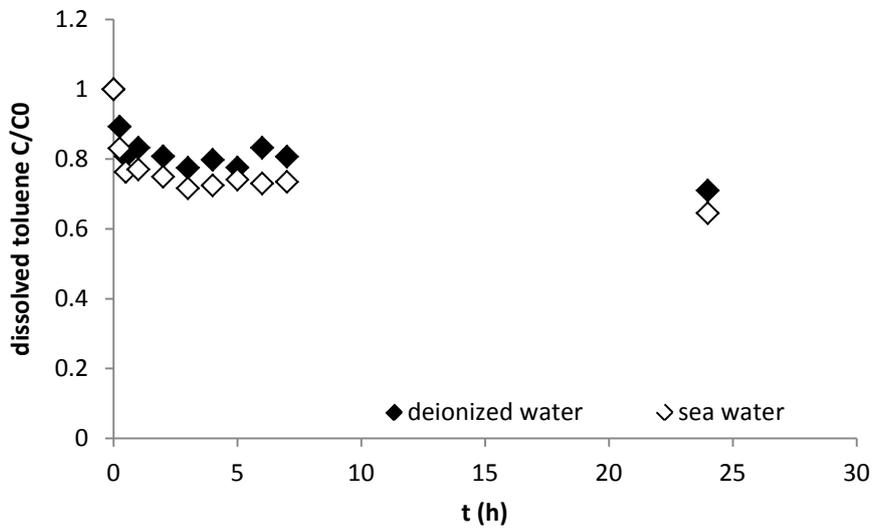

Figure 6   **Kinetic tests with dissolved toluene in deionized and synthetic sea water onto single-walled carbon nanotubes**

The experimental results have clearly shown that ionic strength has no influence on the sorption kinetics for all the materials. The sorption equilibrium is in fact generally quickly reached in both solutions and the toluene equilibrium concentration depends on the initial amount of toluene and the adsorption capacity of the different materials. The equilibrium is faster reached for BC, MWCNTs and SWCNTs probably due to their higher specific surface area related to their powder form.

7.2 Toluene adsorption Isotherms

Experimental isotherms were determined for each of the sorbents which have shown a significant adsorption capacity during the kinetic tests (AC, AC Carbone Italia, OC, BC, MWCNTs, SWCNTs). The experimental results are reported below as amount of toluene adsorbed at equilibrium (S_{eq}) as a function of equilibrium toluene dissolved concentration (C_{eq}) (Figure 7to Figure 12).
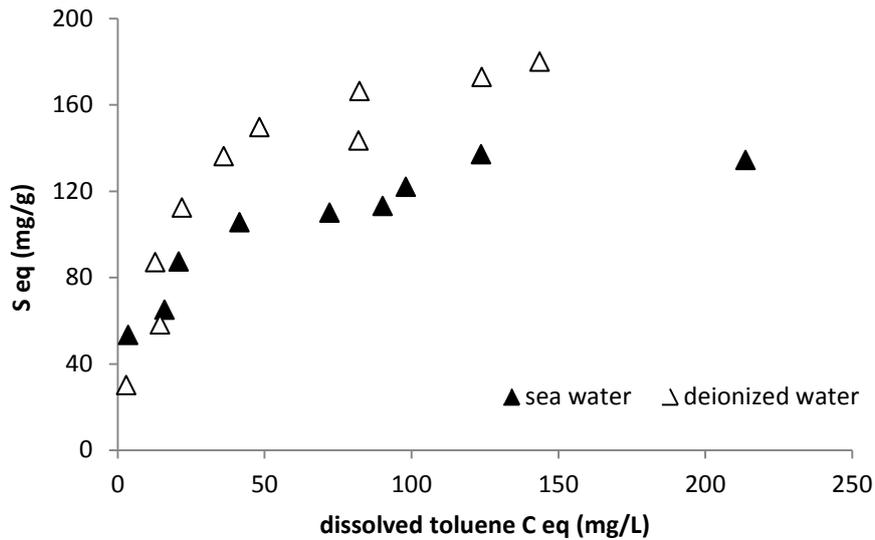

Figure 7   **Sigma Aldrich Activated Carbon (SA AC) isotherms in deionized and sea water**
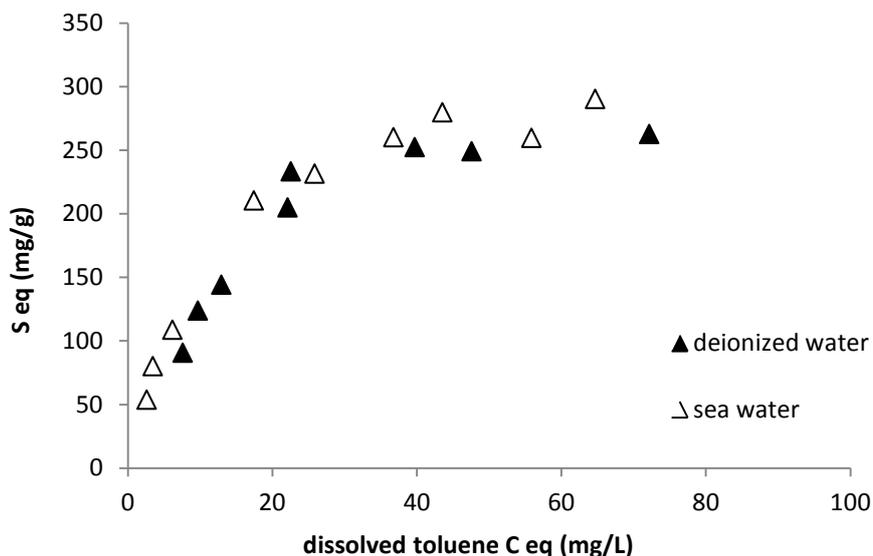

Figure 8   **Carbone Italia AC isotherms in deionized and sea water**

Sigma Aldrich AC and the *Carbone Italia* AC isotherms exhibit a Langmuir type shape with Carbone Italia AC characterized by a higher maximum toluene adsorption than the pure Sigma Aldrich AC. The increase in the salinity of the aqueous solutions seems not to affect the Carbone Italia AC isotherm

whereas Sigma Aldrich AC maximum adsorption was slightly higher in sea water than in deionized solution. The small influence of the salinity on the adsorption capacity suggests that adsorption should be mostly driven by the strong affinity of the activated carbon surface for the toluene which makes negligible the change in the chemical-physical properties of the aqueous solution.
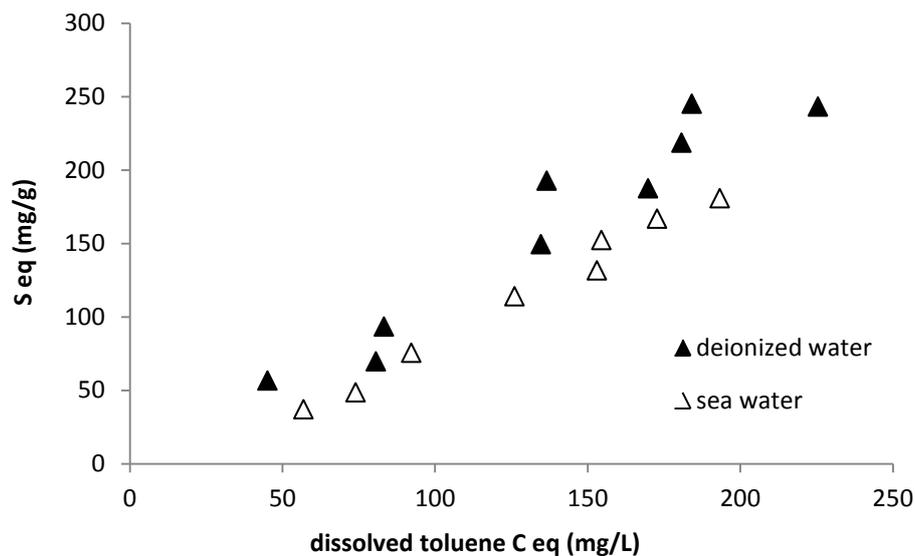

Figure 9 Organophilic clays isotherms in deionized and sea water
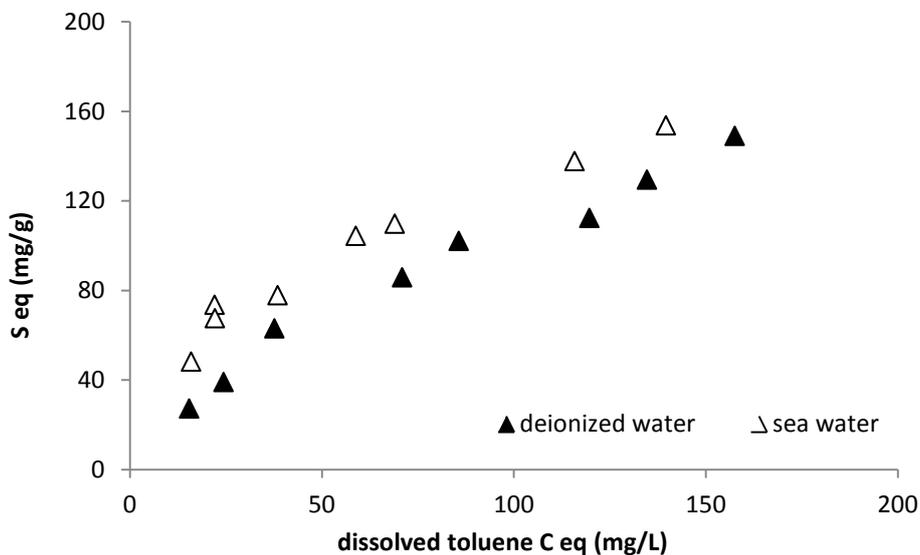
Figure 10 Biochar isotherms in deionized and sea water

Also in the case of OC and BC salinity does not influence the toluene adsorption. Differently from AC, both materials exhibit a quasi-linear behavior. Toluene adsorption isotherm is clearly linear on OC and in the experimental investigated range adsorption is apparently still far from the maximum adsorbable amount. The BC isotherm shape is not perfectly defined, but also in this case Biochar is still far from the maximum adsorbable amount. From these results the use of BC appears very

promising compared to the more consolidated materials, AC and OC, which have to be produced ad hoc for this type of application.
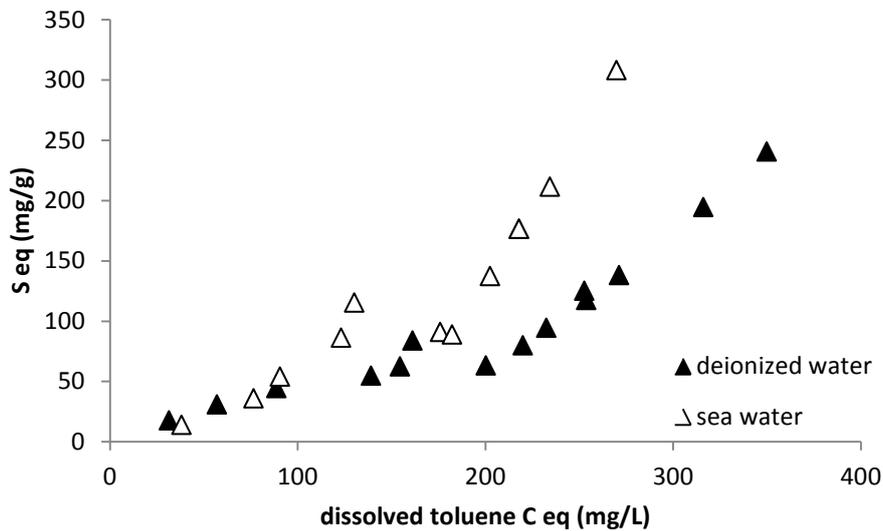

Figure 11   Multi-walled CNTs isotherms in deionized and sea water

Differently, adsorption on MWCNTs seems to exhibit Freundlich type behavior. At low toluene concentration adsorption on the material does not seem favored but after some toluene is sorbed the surface appears more adsorptive. Salinity does not show a dissolved toluene significant effect on the adsorption.
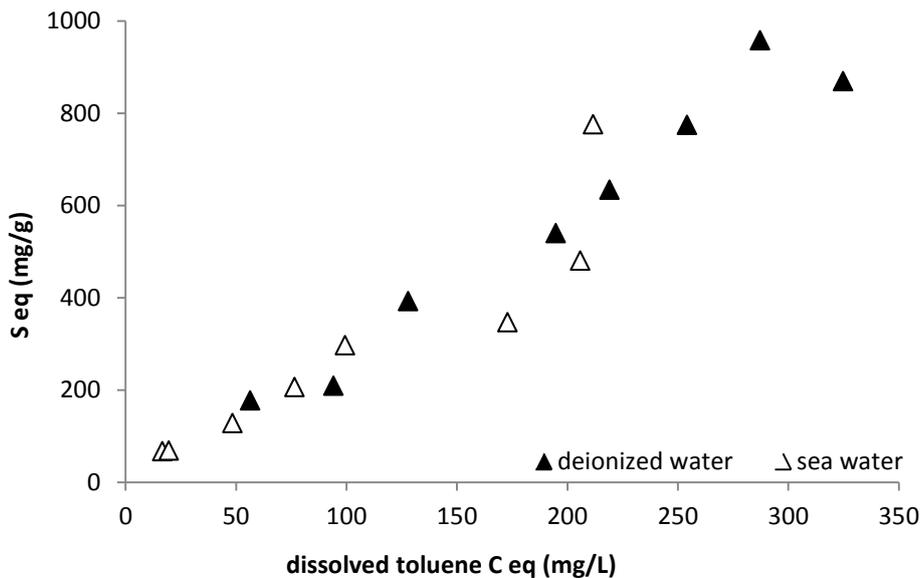

Figure 12   Single-walled CNTs isotherms in deionized and sea water

From the experimental results, toluene adsorption of onto SWCNTs is not affected by salinity. The adsorption capacity is significantly higher than that of MWCNTs. This is probably due to the larger

available surface (all the superficial carbon atoms are exposed and available for adsorption). The adsorption isotherms seem to be linear and in the experimental range of investigated concentration, adsorption capacity is not affected by the concentration of dissolved toluene. SWCNTs have shown the highest removal properties than the other tested materials. At the highest experimental liquid concentration the removal is higher than 95% (w/w).

8   Sorption tests with crude oil

Sorption tests were carried out for five sorbents - montmorillonite clay (Keramost a.s.; Czech Republic), mesoporous alumino-silicate, bio-char, peat moss ((Agros; Czech Republic) – dried in 80°C for 48 hours and sieved for size distribution, in tests fractions with particle size 2.5 – 0.63mm, 0.63-0.2mm and smaller then 0.2mm were used) and powdered activated carbon (Penta s.r.o.; Czech Republic). Tests were carried out with Danish Underground Consortium light crude oil (Københavns Universitet (UCPH)). Sorption equilibrium time was determined via the measurement of time necessary for crude oil sorption and subsequently the crude oil sorption as a function of the amount ratio crude oil: sorbent.

8.1   Time dependence of crude oil sorption

For testing crude oil sorption as a function of contact time, 0.01g of crude oil was weighted into glass bottle. Four mL of deionized water (pH 5.0 ± 0.1) or artificial sea water ASTM D1141-98 (2013)(pH 8.2 ± 0.1) was added and after one day (10°C; 130 RPM) 0.01 g of sorbent was added. Sorbent was mixed (130 RPM; 10°C) with crude oil for 0; 0.5; 1; 1.5; 2; 3; 4; 6 and 24 hours. After that, bottles were centrifuged (5,000g; 10 min) and supernatant was extracted into 3 ml of toluene (30 min; 130 RPM; 28°C). The amount of crude oil in toluene extract was measured spectrophotometrically (420 nm) and the quantity of crude oil determined on the basis of the calibration curve. As controls were measured toluene extracts of deionized water/artificial sea water, extract of all tested sorbents in deionized water/artificial sea water all without addition of crude oil and also clear toluene prepared same way as samples for testing time dependence of crude oil sorption.

Sorption was determined as percentage of crude oil sorbed to sorbent relative to initially added crude oil as shown in the following equation:

$$\text{Sorption}\left[\%\right] = 100 - \left(\frac{m_s}{m_0} \cdot 100\right)$$

m_s – amount of crude oil in solution after incubation with sorbent [g]

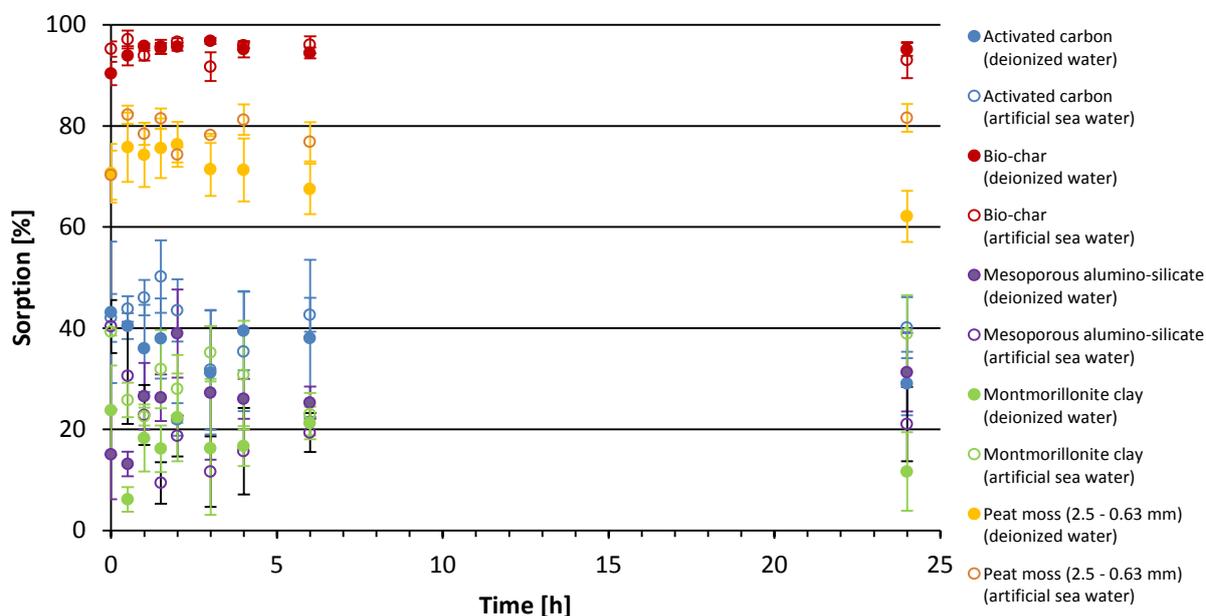m_0 – amount of crude oil initially added [g]

Figure 13   Crude oil sorption as a function of time for different sorbents at 10°C. Values are average from three measurements and error bars represent standard deviation.

Figure 13 shows that in tested conditions bio-char and peat moss possess the best sorption capacities approximately 90% and 70%, respectively. Other tested sorbents had sorption between 20% and 40%. From these experiments time to reach equilibrium of crude oil sorption was one and half hour.

8.1   Dependence of crude oil sorption on amount ratio, crude oil: sorbent

Sorption was measured as a function of crude oil : sorbent amount ratio. Amount of initially added crude oil was 0.01 g and amount of sorbent was adapted to obtain different crude oil : sorbent amount ratios (5:1; 4:1; 3:1; 2:1; 1:1; 1:2; 1:3; 1:4; and 1:5). All the other parameters were similar like in measurement of time dependence of crude oil sorption. Time of mixing of crude oil with sorbent was one and half hour, as determined in aforementioned experiment.
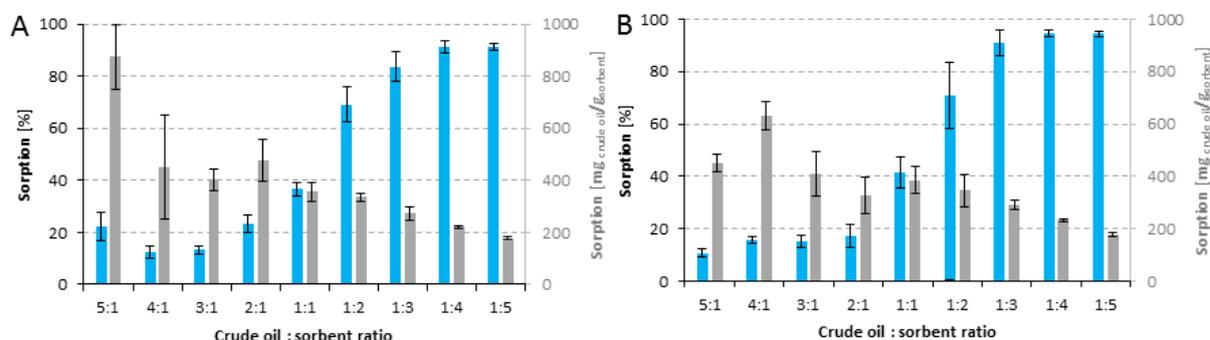

Figure 14   Dependence of crude oil sorption on amount ratio, crude oil: sorbent, for <u>activated carbon</u> in deionized water (A) and in artificial sea water (B).
Light blue bars represent percentage of sorption and light gray bars represent milligrams of sorbed crude oil on grams of sorbent. Average of three measurements with standard deviation.

Figure 15   Dependence of crude oil sorption on amount ratio, crude oil: sorbent, for <u>bio-char</u> in deionized water (A) and in artificial sea water (B).
Red bars represent percentage of sorption and light gray bars represent milligrams of sorbed crude oil on grams of sorbent. Average of three measurements with standard deviation.

Figure 16   Dependence of crude oil sorption on amount ratio, crude oil: sorbent, for <u>mesoporous alumino-silicate</u> in deionized water (A) and in artificial sea water (B).
Purple bars represent percentage of sorption and light gray bars represent milligrams of sorbed crude oil on grams of sorbent. Average of three measurements with standard deviation..
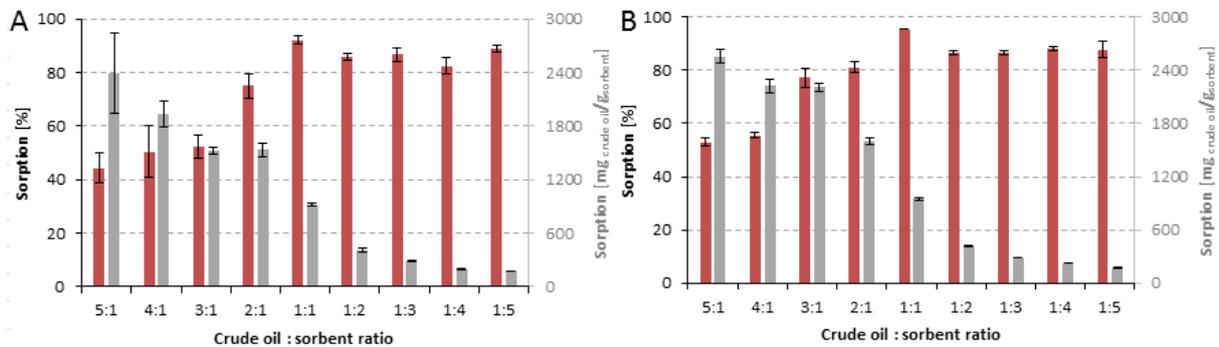

Figure 17   Dependence of crude oil sorption on amount ratio, crude oil: sorbent, for <u>montmorillonite clay</u> in deionized water (A) and in artificial sea water (B).
Light green bars represent percentage of sorption and light gray bars represent milligrams of sorbed crude oil on grams of sorbent. Average of three measurements with standard deviation.
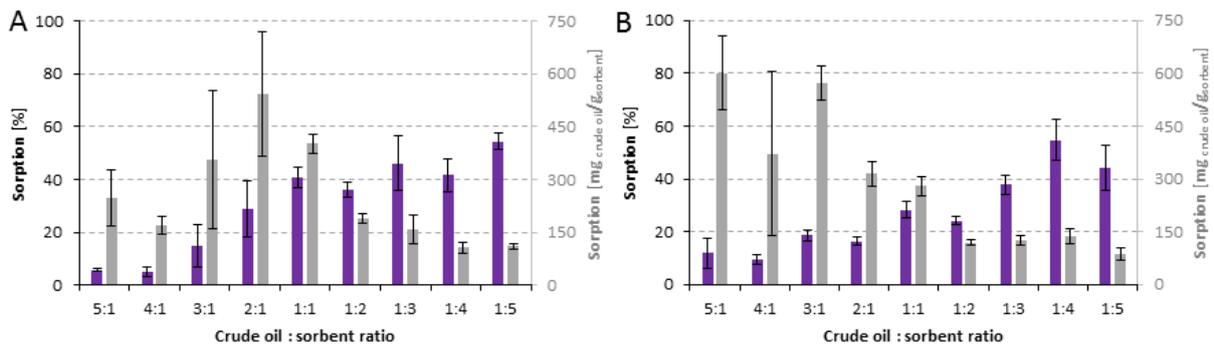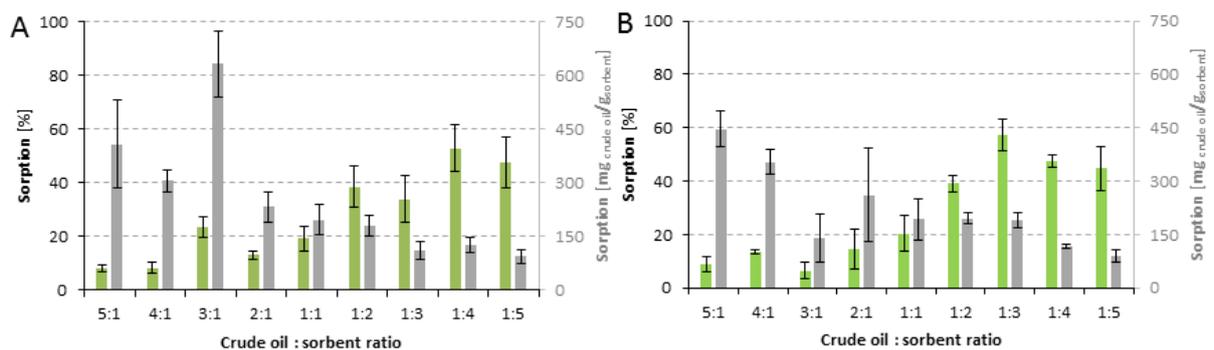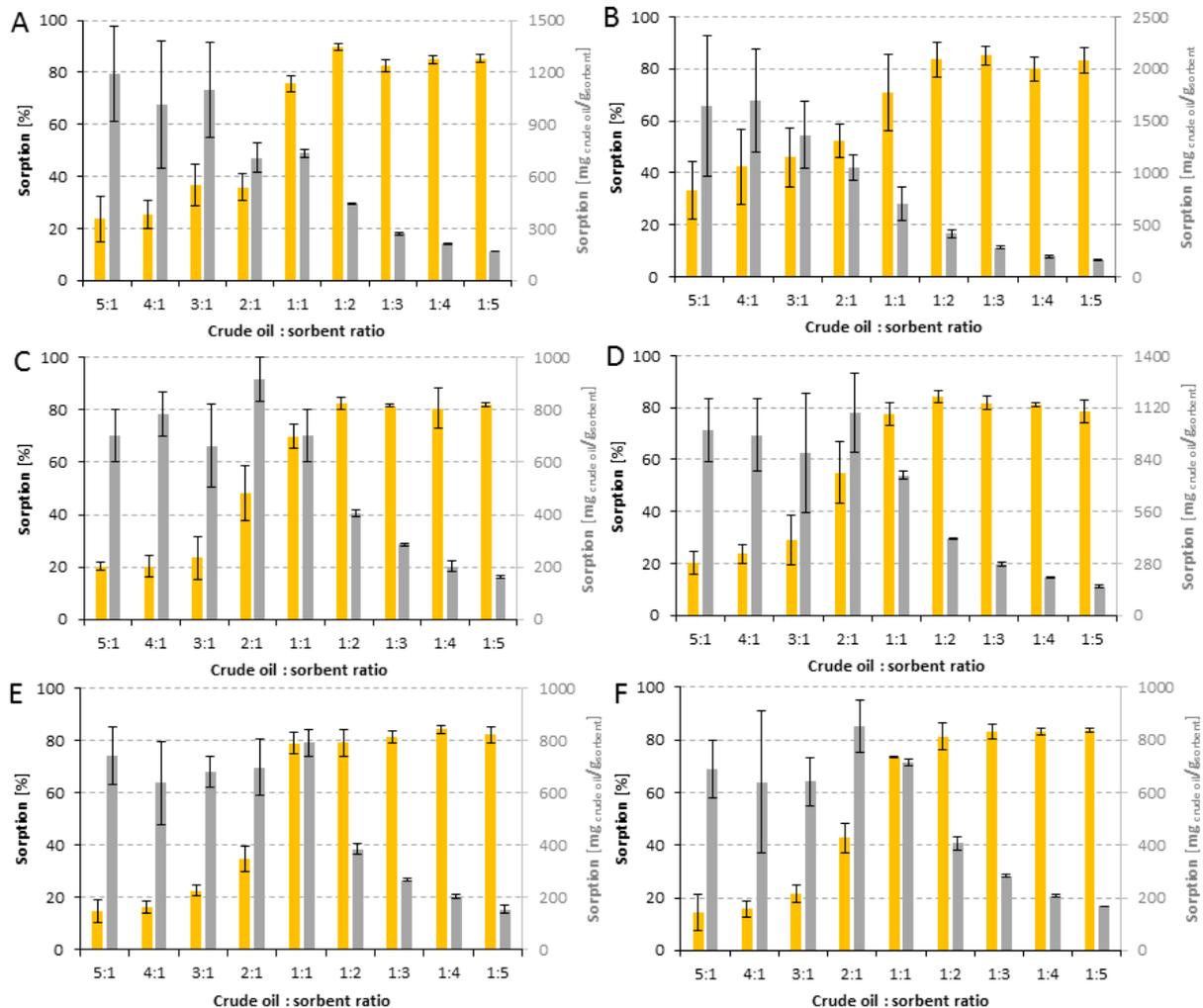
Figure 18   Dependence of crude oil sorption on amount ratio, crude oil: sorbent, for _peat moss_ of different particles sizes.
particle size 2.5 – 0.63mm (A;B), 0.63-0.2mm (C; D) and < 0.2mm (E; F) A; C; E in deionized water and B; D; F in artificial sea water. Average of three measurements with standard deviation.

Figure 14-Figure 18 clearly illustrate that bio-char is the most promising material of all tested sorbents (more than 2 grams of crude oil on gram of sorbent). This sorbent had better sorption capacity than all the others tested sorbents. Second best is peat moss (around 1 g of crude oil on gram of sorbent) and third is activated carbon (around 0.8 gram of crude oil on gram of sorbent). Last two, mesoporous alumino-silicate and montmorillonite clay, have similar sorption capacity around 400 mg of crude oil on gram of sorbent.

Inorganic sorbents, mesoporous alumino-silicate and montmorillonite clay, that were tested proved poor sorption capacity of crude oil. Interestingly the increasing of sorbent amount does not lead into increase of crude oil sorption (crude oil : sorbent amount ratio from 1:2 to 1:5). What could be explained by specific sorption of some components from crude oil, which as it was mentioned above is multicomponent mixture.

All sorbents were tested in deionized water and in artificial sea water. Results indicate that in both, sorption is comparable. Effect of ionic strength, salinity and pH is negligible for all sorbents with exception of peat moss. Peat moss sorption in artificial sea water was higher than in deionized water

(around 20%). In case of peat moss three fractions with different particle size were tested. Sorption capacity was increasing with increasing particle size. What, as we thing, is more driven by surface morphology than by particle size.

Bio-char reach maximal sorption capacity when ratio crude oil : sorbent was between 2:1 and 1:1, for peat moss ratio 1:1 was that with maximal sorption capacity. Activated carbon has this ration shifted to 1:3. This illustrate that for practical use to obtain similar sorption is necessary use double amount of peat moss than bio-char and three times more of activated carbon than peat moss.

9   Conclusion

Understanding the interaction between crude oil and sorbents can improve the knowledge about sorption and desorption of oil from sorbent and can improve sorption capacity. This can make easier choice of appropriate sorbent for combating oil spills.

From the experimental investigation it could be derived how clinoptilolite, graphite, functionalized CNTs, ZVI and PM do not adsorb toluene contamination. Although these materials have no good adsorption property for toluene, their use is still under investigation because they could be used for the adsorption of different type of contaminants, such as heavy metals. Furthermore the materials' tiny size of PM and functionalized CNTs, could be helpful to perform a more effective capping layer by improving the diffusional barrier to the contaminant migration.

Equilibrium experiments have shown that ACs, OC, BC and both CNTs are characterized by an high sorption capacity. AC and OC have been already widely investigated for remediation application. CNTs may be eligible sorbents for organic pollutants removal so they can be tested as potential materials for active capping application. SWCNTs has shown the highest adsorption property with respect to the other investigated sorbent materials. Toluene adsorption was up to 95% as w/w. In the perspective of the re-use of waste materials BC seems to be a very promising materials for HOCs removal; indeed this material have comparable performances with the more consolidated materials such as AC and OC that are commonly used for in situ capping application.

From tests with crude oil, the most promising sorbents were bio-char and peat moss. Their suitability also depends on the type of application, because this sorbents has good buoyancy but after contact with crude oil they start to sink same as activated carbon. Despite their poor crude oil sorption, inorganic sorbents, such as mesoporous alumino-silicate and montmorillonite clay, could be used for nutrient immobilisation for which they might be more suitable than bio-char or peat moss.

Future work will focus on determination of sorption capacity for crude oil at 28°C, on sorbents influence on microbial degradation of crude oil and on amendment of sorbents by nutrients suitable for improvement of microbial degradation of crude oil.

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