

1 Superhydrophobic sponges based on green deep 2 eutectic solvents for spill oil removal from water

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9 KEYWORDS: deep eutectic solvents, oil-water separation, crude oil, melamine sponges

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11 ABSTRACT: The paper described a new method for crude oil-water separation by means of
12 superhydrophobic melamine sponges impregnated by deep eutectic solvents (MS-DES). Due to
13 the numerous potential of two-component DES formation, simple and quick screening of 156 non-
14 ionic deep eutectic solvents using COSMO-RS (Conductor-like Screening Model for Real
15 Solvents) computational model was used. DES which were characterized by high solubility of
16 hydrocarbons and the lowest water solubility were synthesized and embedded on melamine
17 sponges. The new sponges were characterized by Fourier transform infrared spectroscopy (FT-

18 IR), scanning electron microscopy (SEM), X-ray diffraction (XRD), and goniometer. Several
19 parameters affecting the crude oil-water separation (i.e. type and amount of DES, density and
20 porosity of sponges, water contact angle) were thoroughly studied. In order to studies of MS-DES
21 affinity to the selected groups of crude oil i.e. Saturated, Aromatic, Resins, Asphaltenes (SARA)
22 the thin layer liquid chromatography-flame ionization detection (TLC-FID) was used. The
23 obtained results indicate that the melamine sponges impregnated by DES composed of eucalyptol
24 and menthol in 1:5 molar ratio have high real crude oil absorption capacity in the range of 96.1 –
25 132.2 g/g and slightly depends on crude oil compositions, superhydrophobic properties (water
26 contact angle 152°), low density of 9.23 mg/cm^3 , high porosity of 99.39%, and excellent
27 reusability which was almost not changing even after 80 cycles. The outcomes indicate that new
28 MS-DES materials could be excellent alternatives as absorbents for the cleanup of crude oil-
29 polluted water.

30

31 **1. Introduction**

32 During the extraction of crude oil from the bottom of the seas and oceans, as well as accidents
33 of tankers and container ships transporting oil or its products, the leakages and the release of
34 hydrocarbon pollutants into the sea or ocean water may occur [1]. This poses a serious safety
35 concern for the water ecosystem [2,3]. Therefore, there is a serious challenge to clean up oil spills
36 from the surface of the water. Typically, crude oil is removed from water using various methods
37 i.e. in situ burning, chemical dispersants, physical sorption, air flotation, and bioremediation [4–
38 9]. However, most of these methods have some disadvantages i.e. time and energy consumption,
39 high cost, require complex separation steps, and cause the formation of secondary pollution. In
40 addition, the conventional methods are not effective enough.



41 Currently, the physical sorption by means of porous materials has become more and more
42 attractive oil-water separation technique due to its ability to recover and completely remove crude
43 oil from water, without any adverse effect to the aqueous environment. So far, a number of porous
44 materials have been tested as sorbents, i.e. zeolites, activated carbon, wood, porous polymers, clay,
45 silicone gel, graphene aerogel [10–17]. However, some limitations still exist in these sorbent
46 materials including poor sustainability, complicated and expensive preparation process, low
47 selectivity, and recyclability. Ideal sorbent materials should be characterized by high oil absorption
48 capacity, low-cost manufacturing, hydrophobicity, oleiphilicity, selectivity, and long-term
49 reusability [18]. Recently, commercial polymeric sponges (melamine and polyurethane sponges)
50 were considered ideal sorbents due to the low cost, high porosity structure and surface area, high
51 absorption rate, low density, and effective mechanical properties. However, commercial sponges
52 are characterized by hydrophilicity and oleiphilicity nature (absorb both oil and water), which
53 prevents the effective removal of crude oil from the water [19]. Hence, surface modification of
54 commercial sponges is the most promising method for large-scale superhydrophobic, and
55 superoleophilic material preparation [20,21]. The superhydrophobic surface of sponges should
56 have a water contact angle higher than 150° , and low contact angle hysteresis [22].
57 Superhydrophobic surface sponges can be prepared by various methods i.e. dip coating, chemical
58 vapor deposition, in situ chemical reactions, and carbonization [21]. Among the available methods,
59 dip coating is the most widely used for the fabrication of sponge hydrophobic surfaces. This
60 method is simple, fast, and does not require expensive equipment, and it is consists of immersed
61 the sponge several times in the surface-modifying agent's solution and then drying it.

62 The selection of solvents used for the sponge's impregnation process is a crucial parameter.
63 The ideal solvents should be characterized by low solubility in water, high affinity to the

64 hydrocarbon phase, low toxicity, low cost, and easy to prepare [23,24]. Till now,
65 polydimethylsiloxane [25], furfuryl alcohol [26], stearic acid [27], etc. were tested as hydrophobic
66 melamine sponge coating substances. However, there is still a search for greener and perfect
67 solvents. Until recently, due to their unique properties, ionic liquids (ILs) were considered perfect
68 solvents. However, many problems with biodegradability, toxicity, difficult and expensive
69 synthesis were reported which significantly limits the possibilities of their application [28–30].
70 Currently, deep eutectic solvents (DES) are a good alternative to ILs. DES are characterized by
71 similar unique properties to ILs, but their synthesis is much simpler and less expensive. In addition,
72 the application of chemical compounds from natural sources makes DES less toxic and more
73 biodegradable than ILs. Therefore, DESs arouse much attention from both academia and industry
74 [31]. So far they have been successfully used as extraction media [32–36] absorbents [37–41],
75 adsorbent and polymer modifiers [42–44], lubricants [45,46], etc. **However, only one paper**
76 **describes studies on the sponges impregnated by DES for the removal of pesticides and dyes from**
77 **water. In these studies, ionic DES composed of tetrabutylammonium bromide and fatty acids were**
78 **tested as hydrophobic sponge coating [47]. To the best of our knowledge, this is the first study of**
79 **the application of melamine sponges impregnated by deep eutectic solvents for the removal of**
80 **model and real crude oil from water. Most of the research is based on the removal of individual**
81 **substances that may be found in crude oil. Only a few works consider removing real crude oil from**
82 **water. However, there are no studies in the literature that would include studies of the stability of**
83 **the oil composition before and after the absorption from water. This aspect is crucial for the reuse**
84 **of crude oil. In addition, there is no detailed research on the mechanisms of removing individual**
85 **groups of hydrocarbons with the use of MS-based sorbents in the work published so far.**

86 Therefore, in this paper for the first time, the detailed studies on the selection of impregnation
87 layer of MS, explanation of the mechanism of absorption, synthesis and surface properties of new
88 sorbets based on green DES, removal of real crude oil hydrocarbons from water, and stability of
89 crude oil before and after absorption were described. In order to preselect DESs which have the
90 highest affinity to the crude oil components, and the lowest affinity to water, the conductor-like
91 screening model for real solvents (COSMO-RS) was used. Selected DES have been synthesized
92 and used for the melamine sponges impregnation. The surface properties of new superhydrophobic
93 sponges were determined by means of Fourier transform infrared spectroscopy (FT-IR), scanning
94 electron microscopy (SEM), X-ray diffraction (XRD), and goniometer. All parameters affecting
95 the crude oil removal efficiency from water (i.e. type of DES, amount of DES, time of absorption)
96 were thoroughly optimized by means of response surface methodology (RSM) based on a central
97 composite design (CCD). In order to deep studies of MS-DES affinity to the selected groups of
98 crude oil i.e. Saturated (S), Aromatic (Ar), Resins (R), Asphaltenes (A) (SARA) the thin layer
99 liquid chromatography-flame ionization detection (TLC-FID) was used.

100 2. Experimental section

101 2.1. Materials

102 Chemical substances for DES synthesis including camphor (C), menthol (M), thymol (Th),
103 eucalyptol (E), octanoic acid (OA), nonanoic acid (NA), decanoic acid (DA), undecanoic acid
104 (UDA), dodecanoic acid (DDA), citric acid (CA), 4-hydroxybenzoic acid (HA), guaiacol (Gu),
105 and vanillin (Va) with high purity ($\geq 98.0\%$) were purchased from Sigma Aldrich (St. Louis, MO,
106 USA). For the preparation of model crude oil dodecane, cyclohexane, benzothiophene,
107 dibenzanthrone, and quinolone (purity $\geq 99.0\%$) were purchased from Sigma Aldrich (St. Louis,
108 MO, USA). Melamine sponges were purchased from a local supermarket in Gdansk, Poland. For



109 the TLC-FID analysis compressed gases such air (purity N 5.0) generated by a DK50 compressor
 110 with a membrane dryer (Ekkom, Cracow, Poland), and hydrogen (purity N 5.5) generated by
 111 Precision Hydrogen 1200 Generator (PEAK Scientific, Scotland, UK), were used. The following
 112 solvents were used to determine the group composition of crude oil dichloromethane, toluene,
 113 methanol, and hexane (purity $\geq 99.9\%$), which were purchased from POCH (Poland). Solvents for
 114 pretreatment of melamine sponges i.e. acetone, and ethanol (purity $\geq 99.9\%$), were purchased from
 115 POCH (Poland).

116 2.2. Real and model crude oil samples

117 In the studies, twelve types of model and real crude oil samples were analyzed. The samples
 118 of real crude oil came from one of the refineries in Poland. The crude oils were characterized by
 119 the various compositions of the individual hydrocarbon groups including saturated, aromatics,
 120 resins, and asphaltenes (SARA). Model crude oils were prepared by mixing substances
 121 representing individual groups in various volume proportions. In the model mixtures, dodecane
 122 and cyclohexane represented saturated compounds, pyrene - aromatic compounds,
 123 benzothiophene, quinoline - resins, and dibenzanthron - asphaltenes. The detailed compositions of
 124 the model and real crude oils are presented in Table 1.

125 **Table 1** Composition of the crude oil samples

Crude oil samples characteristics	Abbreviation	Saturated hydrocarbons (% w/w)	Aromatic hydrocarbons (% w/w)	Resins (% w/w)	Asphaltenes (% w/w)	Density (g/cm ³) (25°C)
Light crude oil	CO_1	70.8	24.2	4.8	0.2	0.7635
Light crude oil	CO_2	72.0	22.3	5.0	0.7	0.7945
Medium crude oil	CO_3	62.1	19.8	14.7	3.4	0.7942

Medium crude oil	CO_4	72.3	18.2	8.1	1.4	0.7245
Heavy crude oil	CO_5	39.9	24.9	30.9	4.3	0.7867
Heavy crude oil	CO_6	28.1	29	32.7	10.2	0.7914
Model crude oil	MCO_1	80	10	9.5	0.5	0.6901
Model crude oil	MCO_2	70	20	9.5	0.5	0.6960
Model crude oil	MCO_3	50	30	19.5	0.5	0.6987
Model crude oil	MCO_4	40	50	9.5	0.5	0.6997
Model crude oil	MCO_5	20	40	39	1	0.7012
Model crude oil	MCO_6	10	50	39	1	0.7019

126 2.3. Apparatus

127 The following apparatuses were used to evaluate the structural, and morphological properties
128 of superhydrophobic sponges: Tensor 27 spectrometer (Bruker, USA) with an ATR accessory and
129 OPUS software (Bruker, USA); scanning electron microscope FEI Quanta 250 FEG (Thermo
130 Fisher Scientific, Waltham, MA, USA) equipped with an ET detector (Everhart-Thornley
131 Detector, Davis, CA, USA); Rigaku Intelligent SmartLab X-ray diffraction device (Austin, TX,
132 USA) equipped with a sealed x-ray generator; a copper shield operating at 30 mA and 40 kV, a
133 goniometer (OCAH-200 DataPhysics, Germany). **Basic physical properties of DESs and oils were**
134 **measured using a DMA 4100 Density Meter (Anton Paar, Austria), BROOKFIELD LVDV-II +**
135 **viscometer (Labo-Plus, Warsaw, Poland), and a cryostat (HUBER, Edison, NJ, USA).** In order to
136 analyze the group composition of crude oil before and after the absorption process, the thin layer
137 liquid chromatography-flame ionization detection (TLC-FID) technique was used. In the studies,
138 the Iatrosan Mk., silica gel Chromarods S5, TLC TK-8 Chromarods dryer (Iatron Lab., Japan),
139 3200/IS-01 semiautomatic sampler (SES, Germany), AD converter, and corresponding software
140 (Chomik, Poland) were used.

141 **2.4. Procedures**

142 2.4.1. Screening of DES

143 In the studies, screening of 156 non-ionic deep eutectic solvents was prepared by means of the
144 ADF COSMO-RS program (SCM, Netherlands). The geometry optimization of DES composed of
145 two chemical compounds (menthol, camphor, thymol, eucalyptol, octanoic acid, nonanoic acid,
146 decanoic acid, undecanoic acid, dodecanoic acid, citric acid, 4-hydroxybenzoic acid, guaiacol, and
147 vanillin) in 1:1 molar ratio was performed using continuum solvation COSMO model at the
148 BVP86/TZVP level of theory. For all DES the geometry optimization was performed in the gas
149 phase to find the most stable conformers, and then vibrational analysis was performed to identify
150 the deep eutectic solvent conformer to correspond to the true energy minimum. Only for the most
151 energetically favorable conformer, full geometry optimization of DES was performed.

152 Solubility of selected crude oil components in DES (x_j) were calculated using Eq (1):

153
$$\log_{10}(x_j) = \log_{10} \left[\frac{\exp(\mu_j^{hyd} - \mu_j^{DES} - \Delta G_{j, fus})}{RT} \right] \quad (1)$$

154 where:

155 μ_j^{hyd} – chemical potential of pure hydrocarbons [$\text{J}\cdot\text{mol}^{-1}$];

156 μ_j^{DES} – chemical potential of hydrocarbons at infinite dilution [$\text{J}\cdot\text{mol}^{-1}$];

157 $\Delta G_{j, fus}$ – fusion free energy of hydrocarbons [$\text{J}\cdot\text{mol}^{-1}$];

158 R - universal gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$);

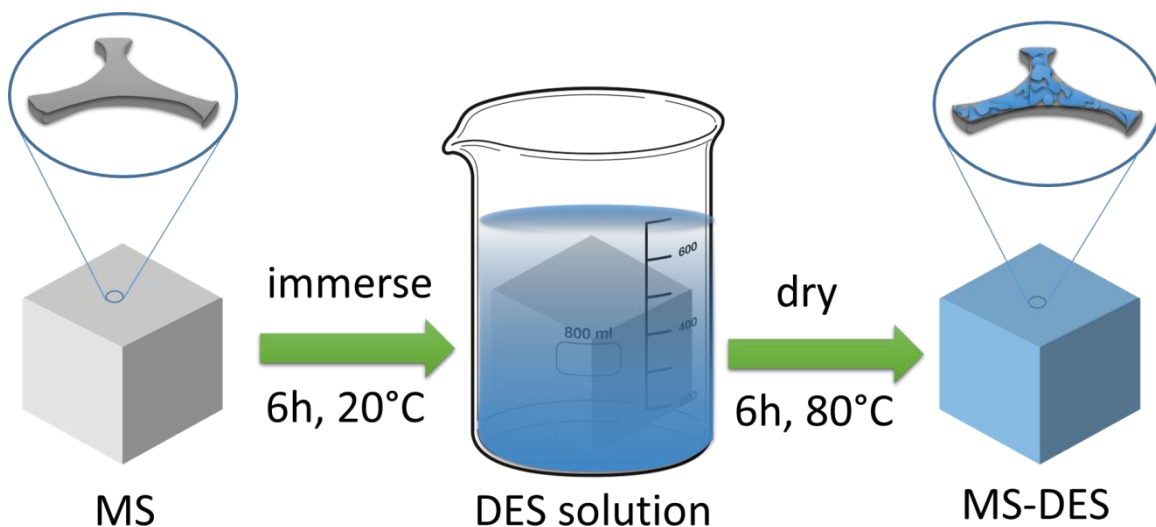
159 T – temperature [K].

160

161 In the screening procedure, the temperature and pressure were set to be the same values as the
162 experimental conditions i.e. 20 °C, and 101325 Pa.

163 2.4.2. Superhydrophobic sponges preparation and characterization 164

165 DES were synthesized by mixing two chemical compounds in 1:1 molar ratio, for which the
166 highest affinity for the hydrocarbon phase and the lowest for the water phase were obtained during
167 the COSMO-RS modeling stage. The synthesis was carried out at the temperature of 80°C and
168 1000 rpm until the homogeneous solution was obtained. Before the mixing procedure, all
169 compounds were dried in a vacuum oven. For liquid DES, densities, and viscosity at room
170 temperature, and melting point was determined according to the procedures from the previous
171 studies [48]. In order to remove oxides on the surface, melamine sponges were first cleaned in
172 ethanol and acetone using an ultrasonic bath and dried at 80°C in a vacuum oven. The sponge was
173 cut into pieces measuring 2.5 x 2.5 x 5.5 cm. In the next step, MS have immersed in 10% DES
174 solutions in ethanol (6 hours) and dried at 80°C for 6 hours. After this time, the DES settled evenly
175 on all parts of the melamine sponge. The scheme of the MS-DES preparation procedure is shown
176 in Figure 1.



177

178 **Figure 1** Schematic illustration of the MS-DES preparation.

179 Pure and DES impregnated melamine sponges were characterized by various techniques.

180 The surface morphologies of MS and MS-DES were studied by means of scanning electron

181 microscopy (SEM). The XRD was applied to confirm the chemical modifications of sponges. MS-

182 DES were studied in the range of 5 to 80° in steps of 0.01°. The speed of sample scanning was

183 1°/min. The form of the sponges was determined in the vertical direction to the corresponding

184 lattice plane. The peak with the highest intensity was used for the quantitative analysis by means

185 of the Reference Intensity Ratio method [49]. Fourier transform infrared spectroscopy with

186 attenuated total reflection (ATR-FTIR) analysis was used for the characterization of functional

187 groups on the MS network. The following parameters was used: spectral range from 4000 to 600

188 cm^{-1} ; number of background and sample scans - 256; resolution - 4 cm^{-1} ; slit width - 0.5 cm. The

189 water contact angle (WCA) of sponges was measured using a goniometer. Measurements were

190 carried out at room temperature. The thermogravimetric analysis (TGA) of MS-DES was prepared

191 according to previous studies [44]. **The tests were conducted in pure nitrogen with a 100 mL/min**

192 **flow rate in the range of temperature from 35 to 1000 °C. The temperature was increased by 10**

193 °C/min. For each sponge sample, three measurements were made at various locations on the
194 surfaces.

195 The density and porosity of MS and MS-DES were measured based on previous studies
196 [50]. The density (ρ) was calculated using Eq. (2):

$$197 \quad \rho = \frac{m_0}{V_0} \quad (2)$$

198 where: m_0 – mass of MS or MS-DES [g];

199 V_0 – Volume of MS or MS-DES [g].

200 The porosity (P) of sponges was calculated using Eq. (3):

$$201 \quad P = \left(1 - \frac{\rho}{\rho_{bmr}}\right) \cdot 100\% \quad (3)$$

202 where: ρ_{bulk} – bulk melamine resin density ($\rho_{bmr} = 1.51 \text{ g/cm}^3$).

203 All measurements were made in triplicate. The mean of the replicates was taken as the target value.

204

205 2.4.3. Oil-water separation procedure

206 The total absorption capacity test was performed by the weighing method, based on previous
207 studies [51]. Sponges were weighed on an analytical balance, and then sponges were immersed
208 into the crude oil. After one minute, sponges with crude oil were weighed again. Three replicates
209 were measured for each value. The absorption capacity of sponges (ΣQ) was calculated using Eq.
210 (4):

$$211 \quad \Sigma Q = \frac{m_1 - m_0}{m_0} \quad (4)$$

212 where: m_1 – mass of the saturated sponge at the absorption equilibrium [g];

213

214 For the studies on the selected hydrocarbon groups' absorption capacity, the concentration of S,
215 Ar, R, A in pure crude oil and crude oil after absorption by MS-DES and squeezing process were
216 measured using TLC-FID based on standard test method IP 469/01 [51]. The absorption capacity
217 for selected hydrocarbons (Q_i) were calculated using Eq. (5):

$$218 \quad Q_i = \frac{C_1 - C_0}{C_0} \quad (5)$$

219 where: C_1 – Selected hydrocarbons group concentration in raw crude oil [%];

220 C_2 – Selected hydrocarbons concentration in crude oil after sponge squeezing [%].

221 After the absorption process, the reusability of MS-DES was studied by repeated absorption-
222 desorption gravimetric measurements consisting of 50 runs, based on the previous studies. In all
223 cycles, the DES-MS was immersed in 50 mL of crude oil (model and real) for 60 sec. and weighted,
224 and then squeezed to extract the absorbed crude oil. The desorption efficiency (R) was calculated
225 by the following Eq. 6.

$$226 \quad R = \left(1 - \frac{m_3}{m_1}\right) \cdot 100\% \quad (6)$$

227 Where: m_3 - mass of the MS-DES after manual squeezing [g].

228 2.4.4. Central composite design

229 The most important independent variables including time of immersion sponge in crude oil,
230 the concentration of DES in impregnation solution, and HBA:HBD molar ratio was used for the
231 optimization of the real and model crude oil absorption condition. In this proposal, a central
232 composite design model was used. The variables were studied at five different levels including -
233 1.68, -1, 0, 1, and 1.68. The model plan was composed of 20 runs. All experiments were repeated

234 in triplicate. In order to prediction of the optimal point of crude oil absorption capacity, the second-
235 order polynomial model was fitted, to correlate the independent variables. Equation (7) of the
236 quadratic model was used to predict dependent variables:

$$237 \quad Y_k = \beta_0 + \sum_{i=1}^3 \beta_i \cdot X_i + \sum_{i=1}^3 \beta_{ii} \cdot X_i^2 + \sum_{i=1}^3 \beta_{ij} \cdot X_i \cdot X_j \quad (7)$$

238 where: Y_k - predicted dependent variables (real and model crude oil);

239 β_0 – intercept;

240 β_i - linear model coefficient;

241 β_{ii} - quadratic model coefficient;

242 β_{ij} - interaction model coefficient;

243 X_i, X_j - independent variables ($i \neq j$).

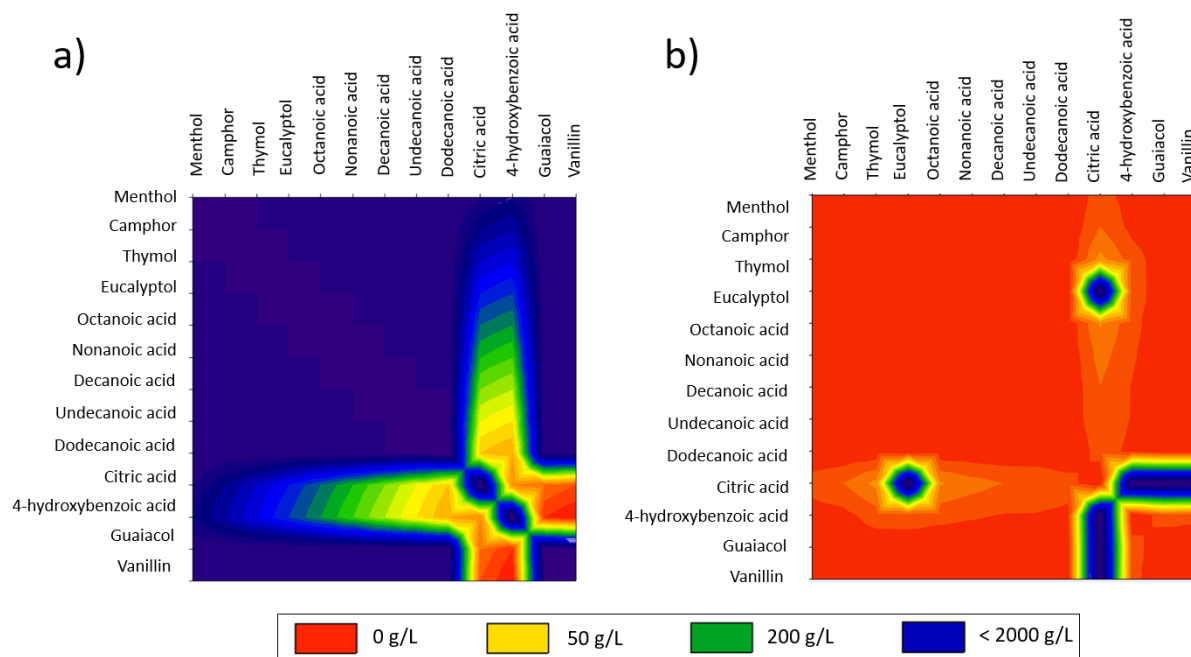
244 **3. Results and discussion**

245 **3.1. Screening of DES**

246 In the studies, screening of 156 non-ionic deep eutectic solvents composed of terpenes (i.e.
247 menthol, camphor, thymol, eucalyptol), carboxylic acids (i.e. octanoic acid, nonanoic acid,
248 decanoic acid, undecanoic acid, dodecanoic acid, citric acid, and 4-hydroxybenzoic acid), and
249 phenols (guaiacol, and vanillin) was prepared by means of the COSMO-RS model. The model
250 included DES in which all the substances mentioned were mixed with each other in a molar ratio
251 of 1:1. The solubility of individual hydrocarbons in DESs, and the lack of water solubility in DESs
252 were chosen as criteria for selecting the best DESs. Among the studied solvents, DES composed
253 of citric acid, and 4-hydroxybenzoic acid, vanillin and guaiacol show high water solubility (higher
254 than 2000 g/L), which is due to the high solubility of individual substances in water. The results
255 indicate that these DES will not be able to form hydrophobic coatings on the surface of melamine

256 sponges. The lowest calculated water solubility represents complexes which were form from
 257 almost insoluble or slightly soluble substances in water i.e. menthol (0.4 mg/L), camphor (1.2
 258 mg/L), thymol (0.9 g/L), eucalyptol (3.5 g/L), octanoic acid (0.68 g/L), nonanoic acid (0.3 g/L),
 259 decanoic acid (0.15 g/L), undecanoic acid (0.023 g/L), dodecanoic acid (0.015 g/L). The second
 260 criterion was affinity of selected hydrocarbons to DES. The results indicate that dodecane and
 261 cyclohexane which represent saturated hydrocarbons in model crude oil have the highest solubility
 262 (<2000 g/L) in DES composed of all terpenes and linear carboxylic acids. In addition, vanillin with
 263 linear carboxylic acids, and terpenes combination show similar dodecane, and cyclohexane
 264 solubility. For the pyrene which represents aromatic components, benzothiophene (resins), and
 265 dibenzanthrone (asphalenes), the similar results were obtained. The only quinoline showed high
 266 solubility in all tested DES (Figures 2, and S1).

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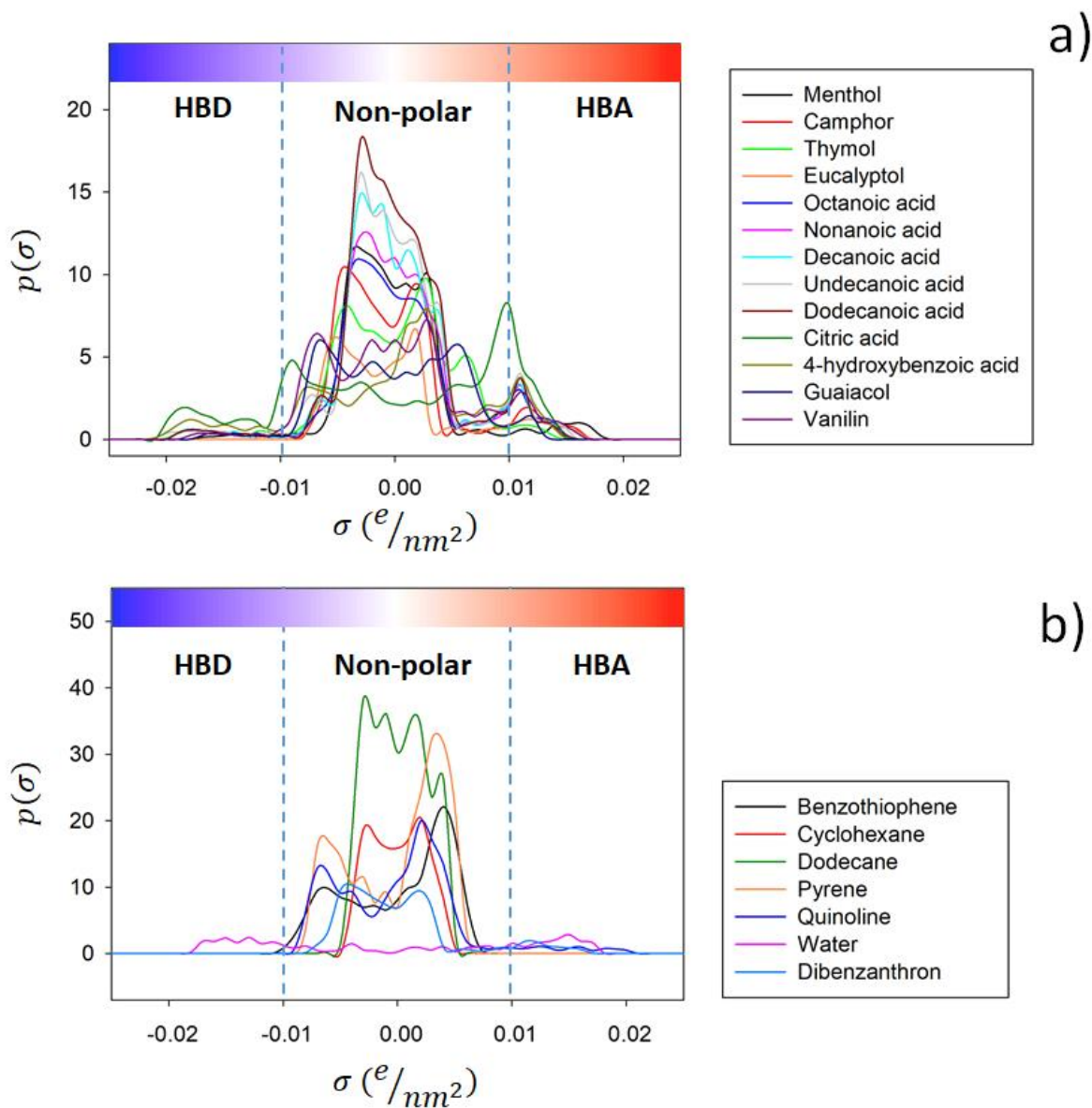


268

269 **Figure 2** Solubility screening of a) dodecane, and b) water in various deep eutectic solvents
 270 complexes in 1:1 molar ratio.

271
272 In order to explanation of the hydrocarbons and water affinity to DES and interpret the
273 interaction between molecules, the charge-related σ -profiles were applied based on the previous
274 studies [37,40]. The σ -profile is one of the most important molecule-specific properties, which can
275 be defined as the probability distribution of surface area with charge density (σ) [52]. In the studies,
276 σ -profiles were present as two histograms, one represents DES components (Figure 3a) and the
277 second – water and selected hydrocarbons (Figure 3b). Both histograms were divided into three
278 regions including hydrogen bond donor (HBD) region in range of $\sigma < -0.0084 \text{ e}/\text{\AA}^2$, non-polar
279 region in range of $-0.0084 \text{ e}/\text{\AA}^2 < \sigma < 0.0084 \text{ e}/\text{\AA}^2$, and hydrogen bond acceptor (HBA) region in
280 $\sigma > 0.0084 \text{ e}/\text{\AA}^2$ range. The obtained results show that all the DES components have the highest
281 peak in the non-polar region (nonhydrogen bond region). Smaller peaks can be identified in the
282 areas responsible for the HBA and HBD properties of DES. From the DES components, camphor
283 and eucalyptol have only a small peak in the HBA area, and there is no peak in the HBD area. This
284 is due to the fact that in their structures only ether ($-\text{O}-$), and carbonyl ($=\text{O}$) groups occur. This
285 indicates that both components play a role as HBA, and there is no possibility of DES formation
286 by mixing each other. Menthol and thymol can be classified to the HBD group of compounds, due
287 to the visible peak in the region below $\sigma < -0.0084 \text{ e}/\text{\AA}^2$, and lack of peak in $\sigma > 0.0084 \text{ e}/\text{\AA}^2$
288 region. Both components contain hydroxyl group ($-\text{OH}$) which are able to the formation of strong
289 H-bonding. Theoretically, linear carboxylic acids including octanoic acid, nonanoic acid, decanoic
290 acid, undecanoic acid, and dodecanoic acid, due to the carboxylic group ($-\text{COOH}$) also should
291 have only one peak in the HBD region. However, a small peak can also be observed in the HBA
292 region. This indicates that carboxylic acids can play both roles as HBA and HBD components.
293 Therefore, they can form DES by mixing with each other and form hydrogen bonds. The rest of
294 the DES components including citric acid ($-\text{COOH}$, and $-\text{OH}$), 4-hydroxybenzoic acid ($-\text{COOH}$,

295 and -OH), vanillin (-O-CH₃, -CHO, and -OH), and guaiacol (-O-CH₃, and -OH) also can play
296 both HBA and HBD role in DES formation. From the model crude oil components, none of them
297 showed a peak in the HBD range. The only dibenzanthron which have carboxylic group, as well
298 as quinoline and benzothiophene which have heteroatoms in their structures show a small peak in
299 the HBA region and a large peak in the non-polar region. The rest of the crude oil components
300 including cyclohexane, dodecane, and pyrene have the only peak in the range in the range of
301 $-0.0084 \text{ e}/\text{\AA}^2 < \sigma < 0.0084 \text{ e}/\text{\AA}^2$ regions. The chart of water indicates that molecules contain only
302 peaks in HBA, and HBD region, and don't have the peak in the non-polar area.
303

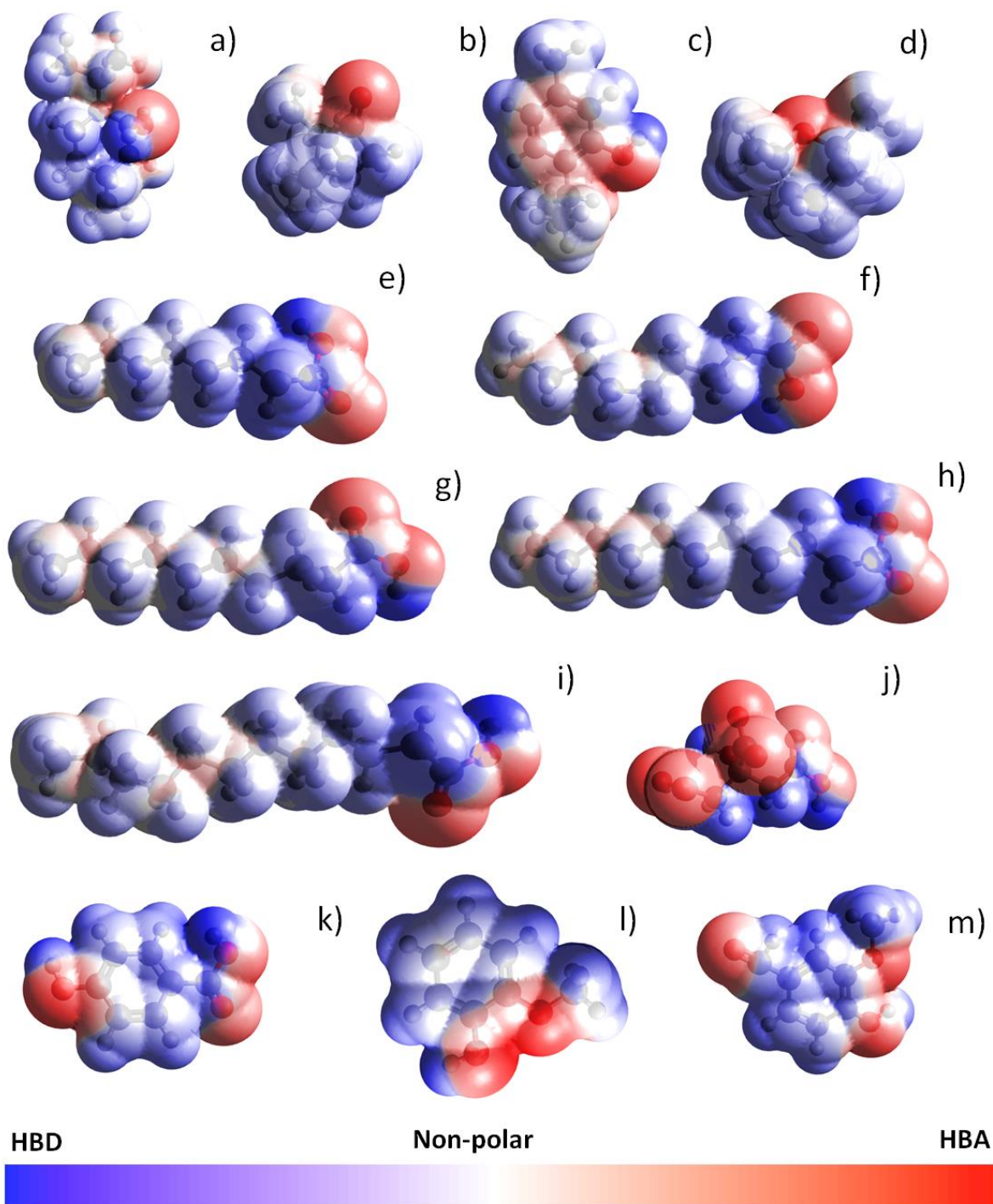


304
 305 **Figure 3** Sigma profile of a) DES components; b) model crude oil components generated through
 306 COSMO-RS model.

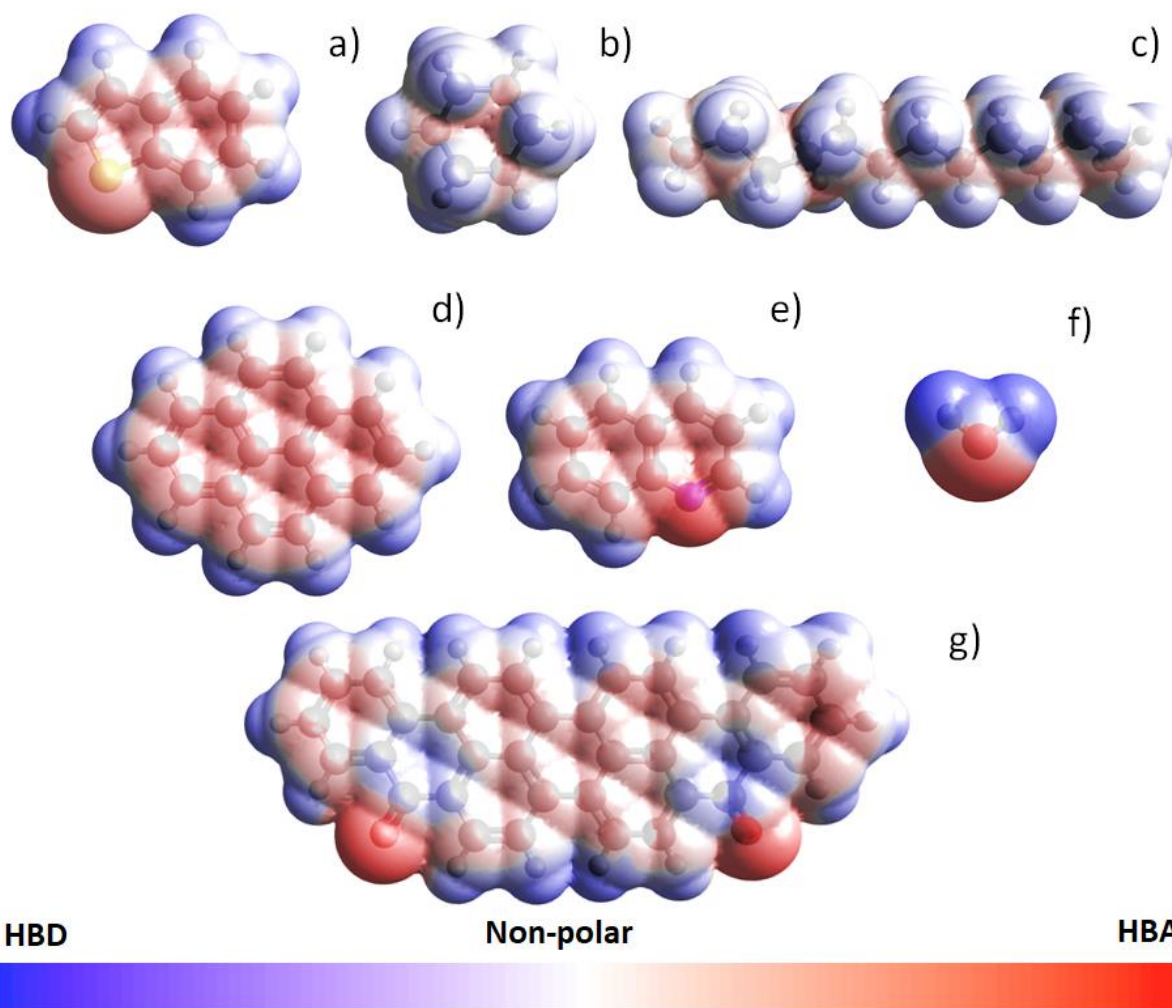
307 In order to the identification of the localization of active groups in DES and model crude
 308 oil components, studies of electrostatic potential (ESP) analysis was performed. Figures 4 and 5
 309 show the ESP of components that are mapped onto electron densities. The blue area on each
 310 component represents positive potential regions, the red area indicates the negative potential, and

311 the white shows a non-polar region in which the potential region is close to zero. In all studied
312 components, the electropositive area is located around the hydrogen atoms in $-\text{COOH}$, $-\text{OH}$, and
313 $-\text{CH}$, $-\text{CH}_2$, and $-\text{CH}_3$ groups. The nonpolar region is located around carbon atoms, and the
314 electronegative area is located close to the oxygen, sulfur, and nitrogen atoms in $-\text{O}-$, $-\text{S}-$, and $-\text{N}-$
315 groups. During deep eutectic solvents' formation, the electropositive region from one of the
316 compounds attracted the electronegative area of the second chemical compound. Then a non-
317 bonded interaction (i.e. H-bonding) formed between the active groups of DES compounds. These
318 interactions are responsible for the formation of stable DES structures with much lower melting
319 points compared to the pure components. The same interactions also are formed during the
320 attachment of DES to crude oil components. Among the crude oil components, particularly strong
321 interactions with DES should be visible for quinoline, benzothiophene, and dibenzanthrone, due
322 to the presence of active groups, i.e. $-\text{N}-$, $-\text{S}-$ and $=\text{O}$ in their structures. For the remaining
323 components of the model crude oil, i.e. pyrene, cyclohexane, and dodecane, only weak red and
324 blue surfaces can be observed. This indicates that a weaker, non-bonded interaction will form
325 between DES and the hydrocarbons.

326



327
 328 **Figure 4** Electrostatic potential maps of DES components: a) menthol, b) camphor, c) thymol, d)
 329 eucalyptol, e) octanoic acid, f) nonanoic acid, g) decanoic acid, h) undecanoic acid, i) dodecanoic
 330 acid, j) citric acid, k) 4-hydroxybenzoic acid, l) guaiacol, m) vanillin.



331
 332 **Figure 5** Electrostatic potential maps of water and model crude oil components: a)
 333 benzothiophene, b) cyclohexane, c) dodecane, d) pyren, e) quinoline, f) water, and g)
 334 dibenzanthron.

335 3.2. DES formation and characterization

336 Based on the COSMO-RS results, only DES which is characterized by high affinity to the
 337 hydrocarbons phase and low affinity to the water phase was synthesized. Therefore, only terpenes
 338 and carboxylic acids were mixed with each other in a 1:1 molar ratio. Some synthesized DES have
 339 already been published. Therefore, basic physical properties (i.e. density, viscosity, and melting
 340 point) which can be affected oil-water separation were studied only for the new DES. All physical

341 data of studied DES (published and new) are presented in Table S1. The obtained results indicate
342 that not all of the 36 proposed two-component complexes form deep eutectic solvents. The melting
343 point of M:UA, M:DDA, C:E, C:DDA, Thy:DDA, OA:DDA, NA:DDA, DA:DDA is higher than
344 25 °C. In the combinations of most of the studied mixtures of monoterpenes with fatty acids, a
345 trend can be observed that with the increase in the length of the aliphatic chain in the acid structure,
346 the melting point increases. Most monoterpenes in combination with DDA acid have a melting
347 point above room temperature. Only eucalyptol forms a eutectic mixture with DDA, the MP of
348 which is 8.5°C. In addition, some monoterpene mixtures also do not form eutectic liquids, i.e.
349 eucalyptol and camphor. This is due to the fact that both components have active oxygen atoms in
350 their structures, which are good acceptors of hydrogen bonds. Nevertheless, the structure of the
351 molecules lacks hydrogen bond donors, which prevents the formation of strong bonds between the
352 components. This is confirmed by the previous considerations.

353 In most processes, the viscosity of solvents should be low as possible to ensure fast process
354 kinetics. It is in line with Walden's rule that the lower the viscosity, the greater the diffusion
355 coefficients, and vice versa. If the viscosity is too high, the mass transfer process is slow and
356 ineffective [53]. On the other hand, higher viscosity can more easily trap DES in the pores of the
357 sponge and stay longer on the sponge surface. However, this can lead to clogging of the pores and
358 reduce the absorption space, and limited the absorption capacity. Therefore, low-viscosity DES
359 should be chosen for the impregnation of sponges. The viscosity of the tested DESs at 25 °C is in
360 the range from 4.4 to 57.9 mPas. The lowest viscosity was obtained for DES composed of
361 eucalyptol. These values were 8.04, 5.25, 5.89, 6.37, 6.8, and 7.16 for E:M, E:OA, E:NA, E:DA,
362 E:UDA, and E:DDA, respectively.

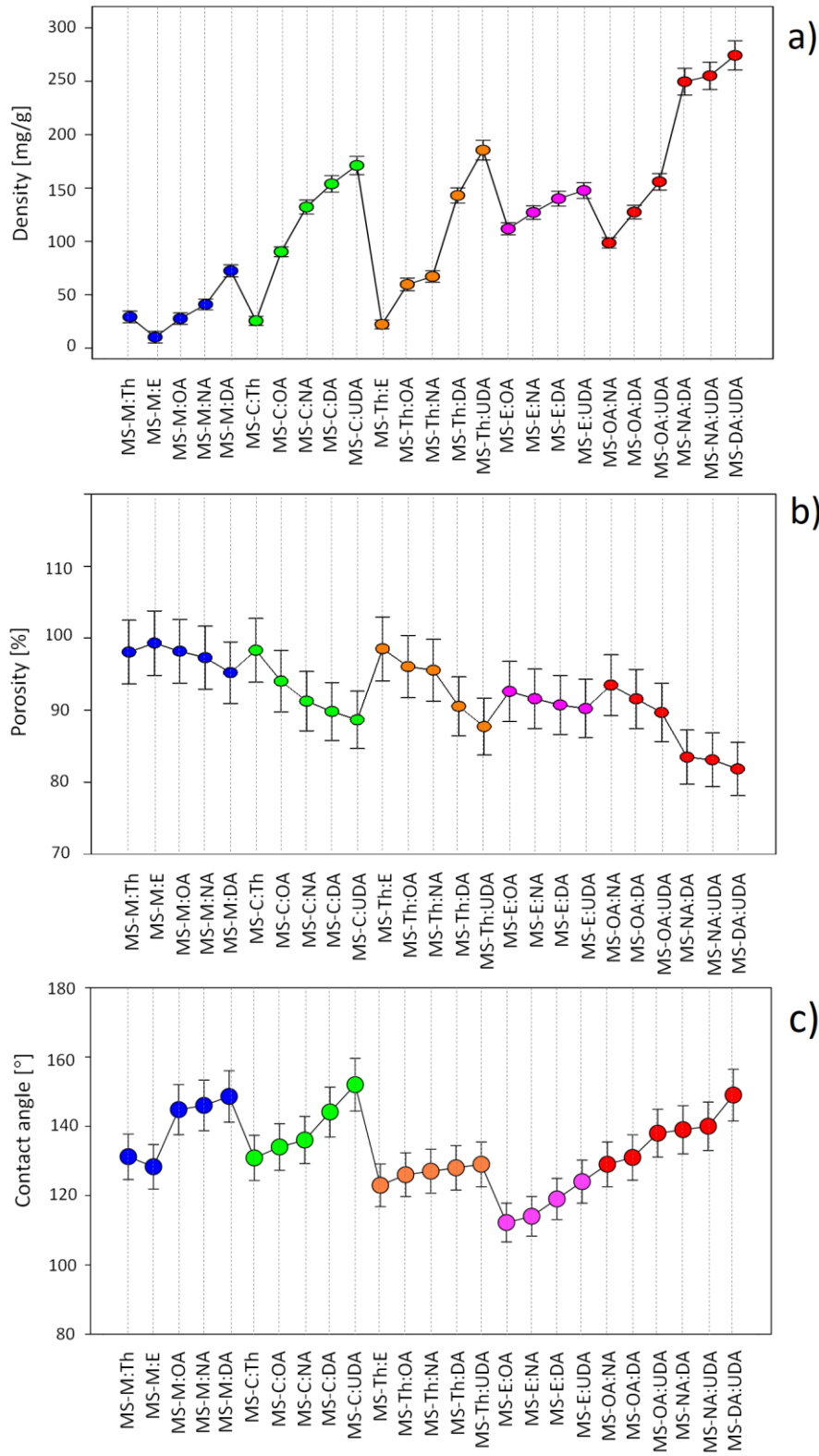
363 The next important DES physicochemical parameter is density. The fact that petroleum
364 hydrocarbons and crude oil have a lower density than water causes them to float on the surface of
365 the water. Therefore, the new DES, which will be used for impregnation, should not have higher
366 densities so as not to flood the sponge. The obtained results of the density of DES indicate that all
367 densities are lower than water. DES densities are in the range of 0.8362 – 0.9873 g/cm³. It can be
368 concluded that all DES fulfill the necessary condition of low density.

369 **3.3. Superhydrophobic sponges preparation and characterization**

370 3.3.1. MS-DES characterization, and pre-selection

371 Only DESs, which were liquids at room temperature, were deposited on melamine sponges.
372 All prepared MS-DES were analyzed with a goniometer to determine the contact angle for water
373 and real crude oil samples. In addition, the density and porosity tests for all the MS-DES were
374 prepared. For preliminary tests, medium real and model crude oil samples (CO_3, and MCO_3)
375 which represent the most popular crude oils composition were used. The obtained studies indicate
376 that all the prepared MS-DES are characterized by hydrophobicity character. The WCA of all
377 sponges was higher than 125° (Figure 6). This is due to the hydrophobic nature of pure DES.
378 Additionally, such results indicate a very thorough impregnation of the melamine sponges. On the
379 other hand, the contact angle of both model and real crude oil was 0° for all 25 MS-DES. This
380 indicates a very good oil absorption capacity of the impregnated sponges. The pure melamine
381 sponge showed high wettability for both water and crude oil, which indicates a hydrophilic and
382 oleophilic character. In both cases, the contact angle was 0°. The density and porosity of sponges
383 are also important parameters that decide the absorption capacity of MS-DES. Theoretically, the
384 greater the porosity and the lower the density, the greater the absorption capacity. The density and
385 porosity of pure MS were 8.72 mg/cm³, and 99.42%, respectively. All sponges were less porous

386 than pure sponges. Among the impregnated sponges, MS-E:M was characterized by the highest
387 porosity (99.32 %), and the lowest density (10.26 mg/cm³). Slightly lower porosity was found for
388 the remaining sponges impregnated by DES composed of menthol. The porosity values were
389 98.07, 98.17, 97.29, and 95.21 % for MS-M:Th, MS-M:OA, MS-M:NA, and MS-M:DA,
390 respectively. These sponges were also characterized by low density. The lowest values of porosity
391 in the range of 81.84 - 93.47% and the highest density in the range of 98.6 – 274.2 mg/cm³ were
392 obtained for MS impregnated with DES composed only of carboxylic acids. The reduced porosity
393 and higher density of impregnated sponges result from the uneven distribution of DES on the
394 surface of the sponges, as well as from the clogging of the pores by DES, which prevents the
395 penetration of crude oil into the sponges [54].

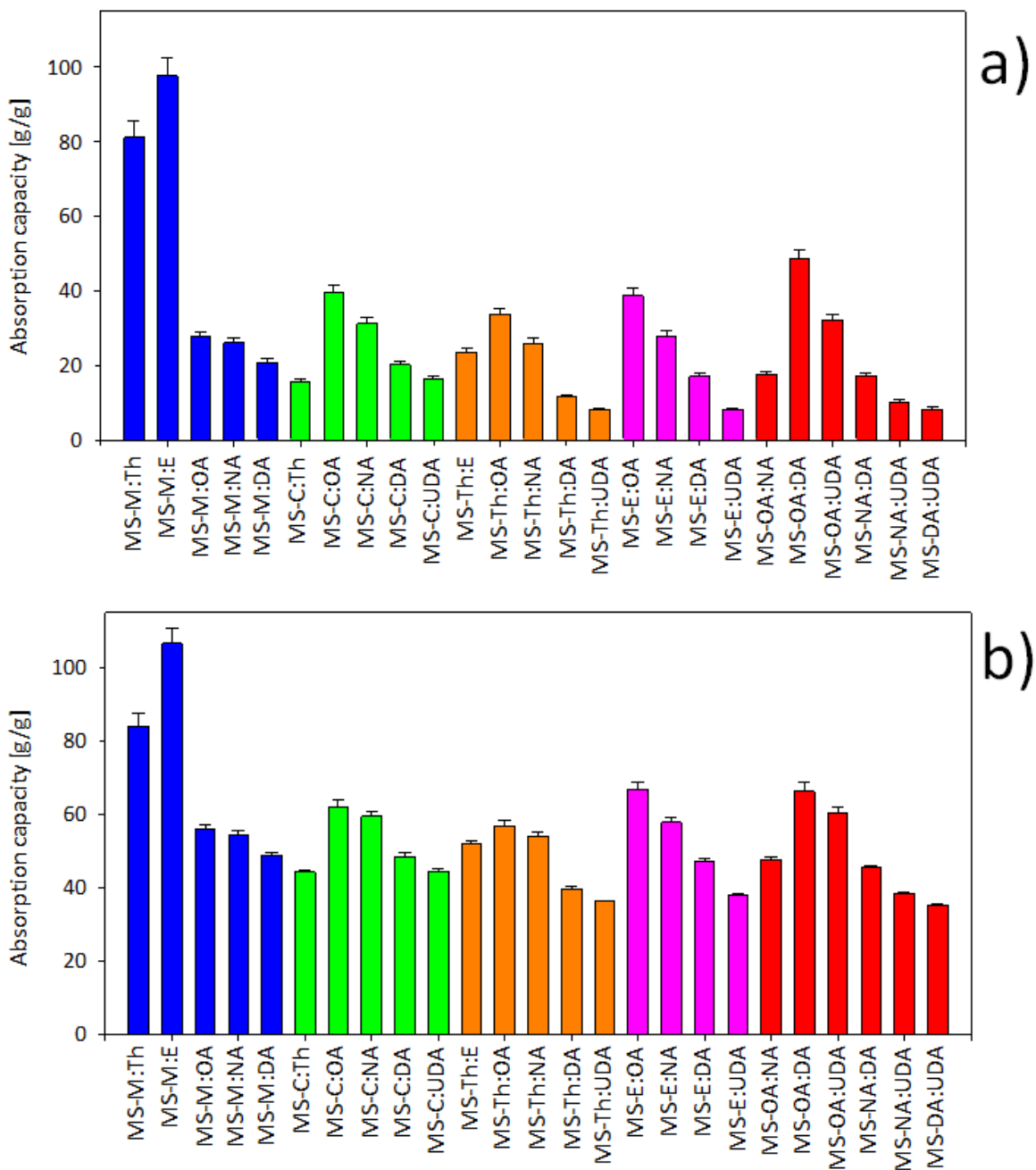


396

397

Figure 6 Density, porosity and water contact angle of MS-DES.

398 In the next part of the studies, the tests of the model and real crude oil absorption capacity were
399 prepared. The obtained results indicate that the MS-E:M and MS-M:Th sponges have the highest
400 absorption capacity, with 97.5 g/g, and 81 g/g capacities values. For the remaining sponges, the
401 values did not exceed the capacity of 50 g/g. Similar results were obtained for model crude oil.
402 The same sponges i.e. MS-E:M, and MS-M:Th were characterized by the highest absorption
403 capacity (112.7 and 83.6 g/g). The results are presented in Figure 7. For a clean sponge, the results
404 of the absorption capacity were very similar to MS-M: E. However, due to the hydrophilic nature
405 of pure MS, it cannot be used to remove oil from water. Therefore, in further studies, only sponge
406 MS-E:M (1:1) which is characterized by hydrophobicity, high porosity, low density, and high
407 absorption capacity of both model and real crude oil were used.



408

409 **Figure 7** Absorption capacity of a) real, b) model crude oil by melamine sponges embedded by

410 DES (MS E:M (1:5)).

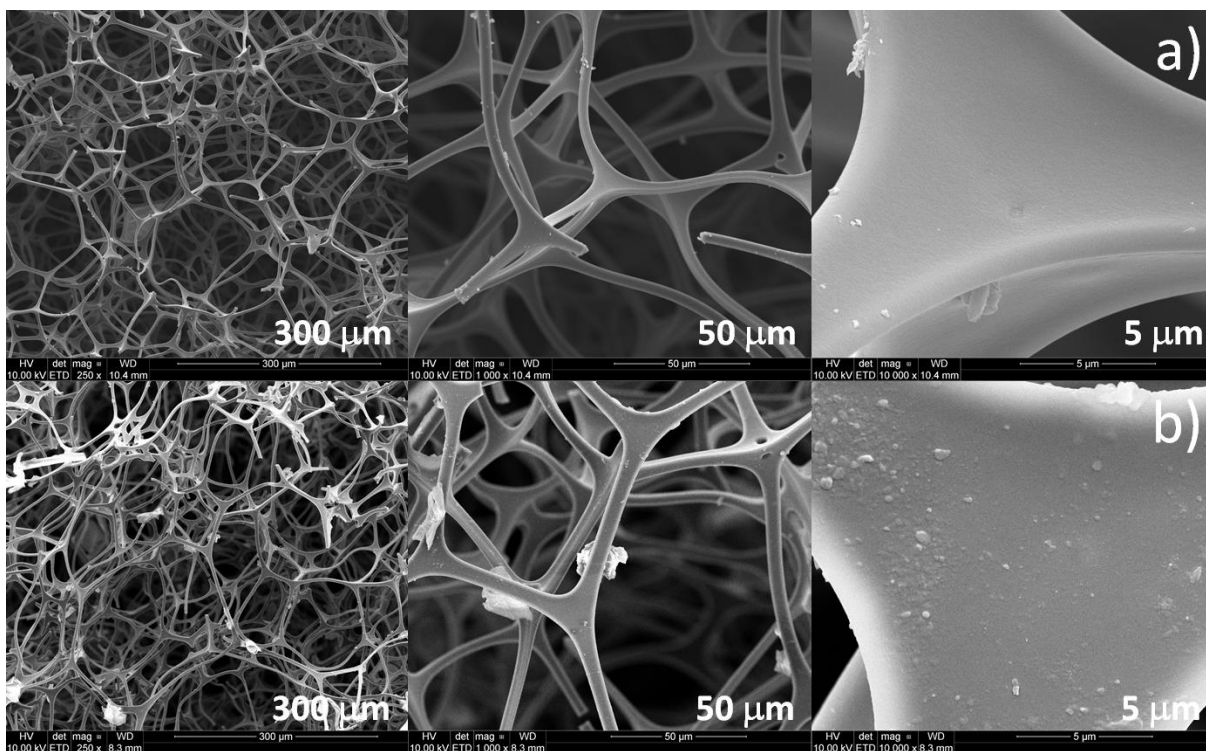
411

412

413

414 3.3.2. SEM analysis

415 In the further part of the studies, the DES composed of menthol and eucalyptol were also prepared
416 in 1:2, 1:3, 1:4, and 1:5 molar ratios, and then they were used to impregnate the sponges. The
417 morphology of the sponges before and after DES impregnation (MS, MS-E:M (1:1), MS-E:M
418 (1:2), MS-E:M (1:3), MS-E:M (1:4), and MS-E:M (1:5)) was studied by Scanning Electron
419 Microscopy with Energy Dispersive X-Ray Analysis (SEM-EDX) measurements. The SEM
420 results are presented in Figures 8 and S2. Figure 8 shows that the melamine sponge before
421 impregnation is characterized by a three-dimensional, hierarchical, and porous structure with a
422 pore size of approx. 80-100 μm and smooth skeleton surface with a diameter of approx. 10 μm .
423 After the impregnation process, the sponges did not change their porous structure (Figure 8, and
424 S2). A slight increase in the diameter of the skeleton can be observed, which indicates a DES-
425 impregnated layer. The pores are not blocked, which is beneficial for the absorption and increased
426 flow of hydrocarbon substances [55]. Additionally, the skeleton surface has become rough after
427 the impregnation process and fine particle clusters can be observed. The particle clusters and thin
428 film on the skeleton surface are responsible for the hydrophobic and oleophilic nature of the
429 sponges.



430
 431 **Figure 8** SEM images of a) pure MS, and b) MS-E:M (1:5).

432

433 The elemental composition of the sponges was studied with EDS. The results of pure MS and MS-

434 E:M (1:5) are presented in Figure 9. The pure MS sponge contains only C, N, and O atoms, which

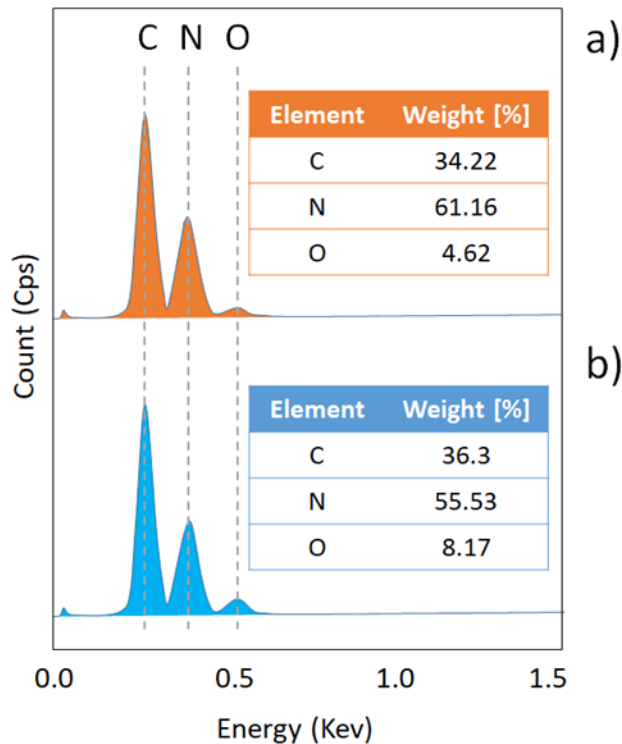
435 is in line with the standard composition of melamine foam [60,61]. In the sponge, after the MS-E:

436 M (1: 5) impregnation process, an increase in the ratio of carbon and oxygen to nitrogen atoms can

437 be observed. This is due to the presence of a DES layer on the surface of the MS skeleton. Similar

438 results were obtained for the remaining sponges (MS-E:M (1:1), MS-E:M (1:2), MS-E:M (1:3),

439 and MS-E:M (1:4)).



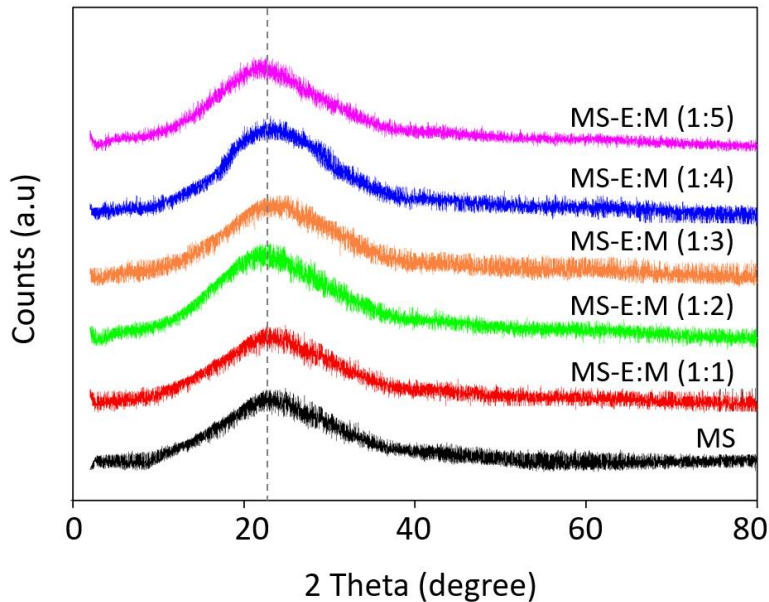
440

441 **Figure 9** Element compositions of a) pure MS, and b) MS-E:M (1:5).

442 3.3.3. XRD analysis

443

444 The microstructures of sponges were studied by XRD analysis. The diffractograms of pure MS
 445 and MS after impregnation in the 2θ interval ranging from 5 to 80° are presented in Figure 10. It
 446 can be seen that pure MS and all MS-DES present broad peak in the range of $10 - 30^\circ$ which
 447 suggest the non-crystalline nature of melamine sponges. According to the literature data, if the
 448 sponges had a crystalline form, then in the diffractogram peaks around 17.4 , 20.6 , 25.3 , 30.6 , 31.6 ,
 449 33.6 , 34.8 , and 44.9° can be observed [56].

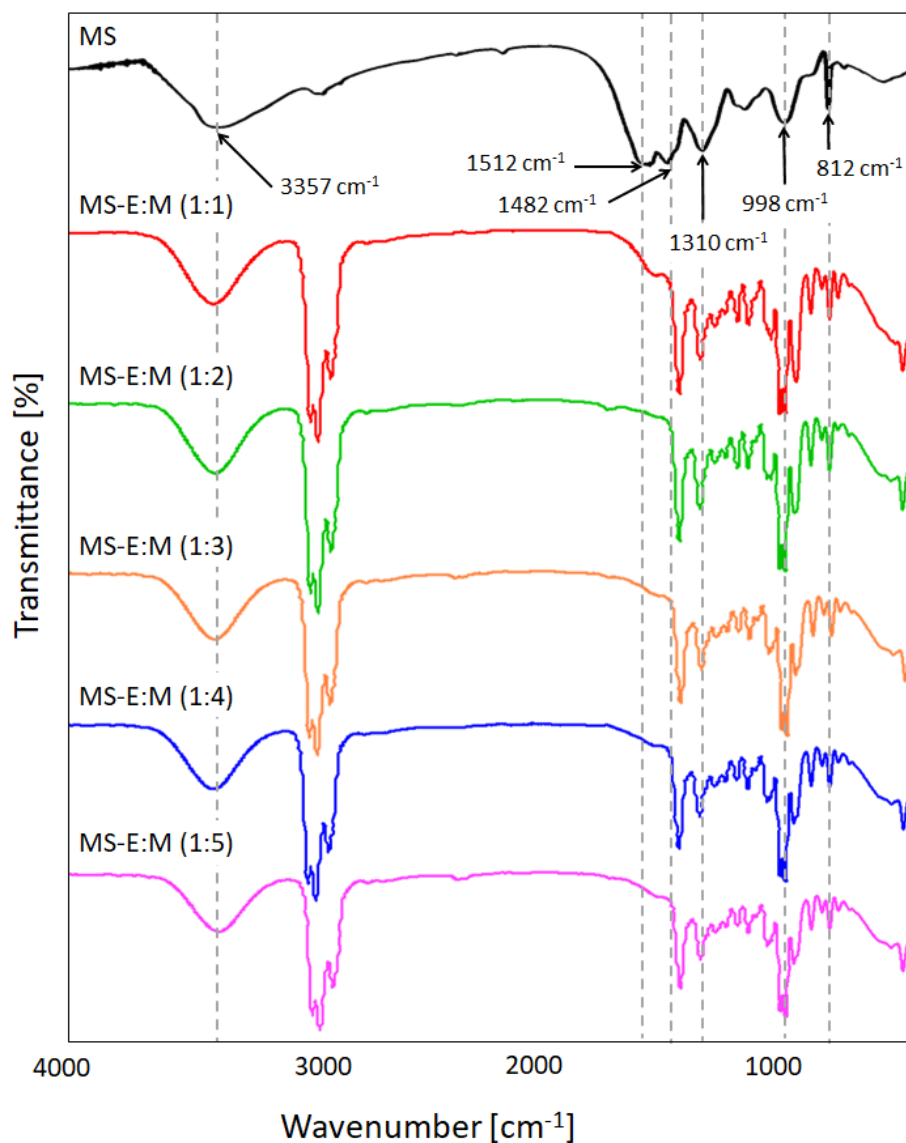


450
 451 **Figure 10** XRD diffractograms of pure MS, and MS after DES impregnation MS-E:M (1:1), MS-
 452 E:M (1:2), MS-E:M (1:3), MS-E:M (1:4), and MS-E:M (1:5).

453 3.3.4. FT-IR analysis

454
 455 For understanding the intermolecular interactions between DES and sponges, ATR-FTIR
 456 spectroscopy was applied. All spectra are presented in Figure 11. In the spectrum of pure melamine
 457 sponge, prominent peaks at 3357, 1512, 998, and 812 cm^{-1} can be observed. These peaks can be
 458 assigned to N – H stretching of the primary and secondary amines, C – N stretching, C – O
 459 stretching, and s-triazine ring bending, respectively. The peaks in 1310, and 998 cm^{-1} indicate the
 460 C–H bending. In addition, two peaks with low intensity can be observed at 2891 and 2827 cm^{-1}
 461 which can be attributed to C–H stretching [57–60]. All identified peaks in the MS spectrum
 462 remained at the same positions in the spectra of the sponges after DES impregnation. On the other
 463 hand, the peak of the N-H group was covered with the peak of the -OH group of menthol. However,
 464 based on previous research, the N-H group should participate in the formation of hydrogen bonds
 465 with DES components [26]. In the spectra of MS-DES, the most intense peaks come from the DES

466 components. The peaks in range from 2951 to 2868 cm^{-1} corresponds to the symmetric and
467 asymmetric CH_2 and CH_3 stretch. The lower intensity peaks at 2920 and 2871 cm^{-1} can be
468 attributed to a methyl group. A broad peak corresponding to a hydroxyl group ($-\text{OH}$) is observed
469 at 3347 cm^{-1} in MS-E:M (1:1) and MS-E:M (1:2). As the menthol content in DES increases, a
470 shift of the peak towards lower values can be observed. Similar behavior was observed for the
471 peak located at 1025 cm^{-1} which is attributed to the C-O bond. This indicates the $-\text{OH}$ group is
472 involved in the formation of hydrogen bonds between M and E, and between M and MS.



473 **Figure 3** ATR-FTIR spectra of pure MS and MS after DES impregnation.

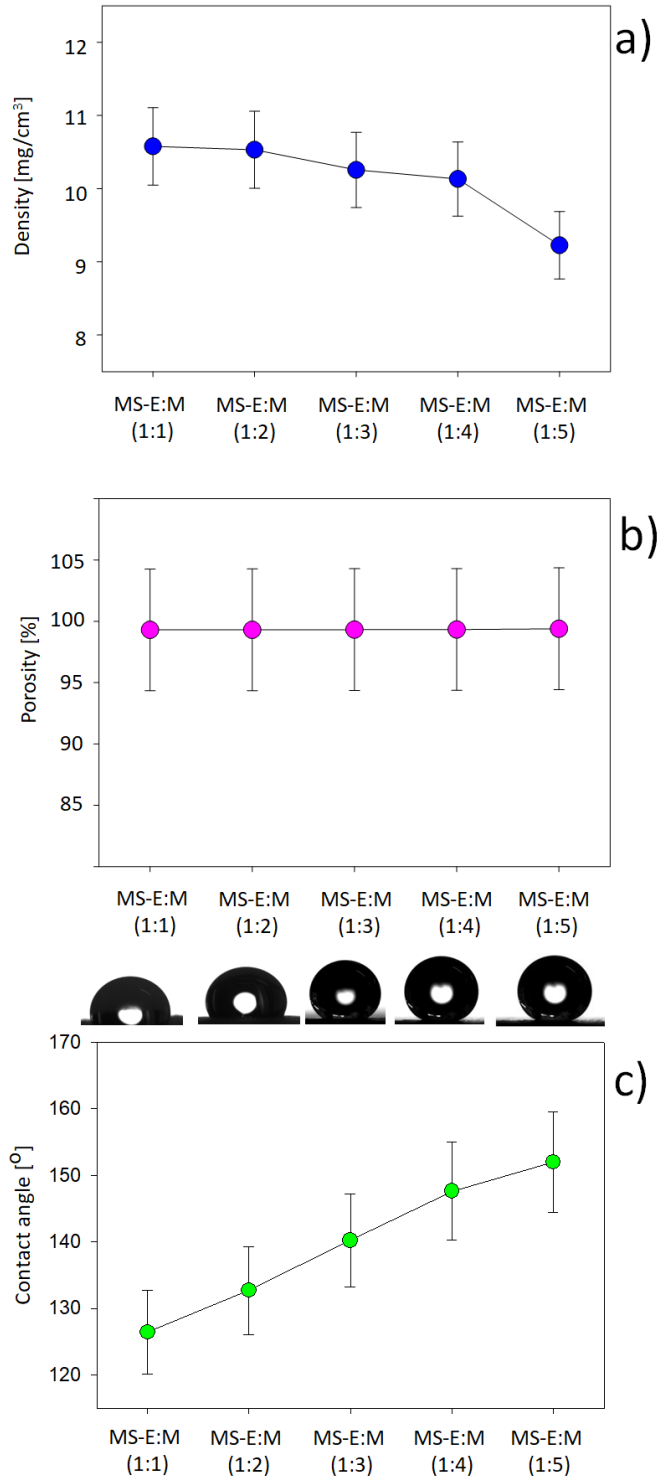
474 3.3.5. Water contact angle, density, and porosity of MS-M:E

475

476 The results of the densities of MS-E:M in various molar ratios, indicate that as the menthol
 477 content in DES increases, the MS-DES density gradually decreases, from 10.58 to 9.23 mg/cm³.

478 The opposite results were obtained for porosity, which is closely related to density. The porosity
 479 increased from 99.3% to 99.39%. However, in the case of both parameters, the changes are
 480 insignificant and are within the standard deviation. They can be considered statistically

481 insignificant. The most important and the greatest change can be observed for the WCA parameter.
482 As the menthol content in DES increased, the contact angle increased from 126° to 152°. The
483 obtained results indicate that after increasing the E:M molar ratio to 1:5, the MS began to fulfill
484 the criteria of a superhydrophobic surface. This is due to the fact that menthol, characterized by
485 lower water solubility than eucalyptol. On the other hand, the crude oil contact angle did not
486 change with increasing menthol content in DES, and for each of the crude oil samples were 0°.
487 These results are also confirmed by the fact that the sponge without modification begins to fall to
488 the bottom of the beaker immediately after being immersed in water, while the sponge impregnated
489 with DES floats on the surface of the water. When both types of sponges with and without
490 impregnation layer were immersed into the beaker with water and crude oil, then both sponges
491 begin to absorb the oil and sink to the bottom of the beaker. This indicates that the clean sponge is
492 hydrophobic and oleophilic, while the modified DES sponge has oleophilic character and excellent
493 water-repelling properties. Similar results were also observed for MS impregnated by furfuryl
494 alcohol, have the WCA 138–145° [26]. All obtained results are presented in Figure 12.



495

496

Figure 4 Density, porosity, and water contact angles of impregnated sponges MS-E:M (1:1),

497

MS-E:M (1:2), MS-E:M (1:3), MS-E:M (1:4), and MS-E:M (1:5).

498 3.4. Optimization of MS-DES parameters

499 3.4.1. Central composite design

500

501 In further studies, the MS-DES which represents the highest crude oil absorption capacity was
502 used in the CCD model. For MS-M:E, the most important parameters were applied to plan a
503 subsequent higher order 2^2 design. Three factors including DES concentration, HBA:HBD molar
504 ratio and time of immersion in the mixture of crude oil-water were used for the optimization. In
505 Table 2 the extended values for all the parameters in five levels are presented. The design matrix
506 and responses for absorption capacity of real and model crude oil are presented in Table S2.

507 **Table 2** Experimental ranges and levels of two variables in CCD.

Variables	Ranges and levels (star points = $(2^k)^{1/4} = 1.682$) ^{a)}				
	$-\alpha$	-1	0	+1	$+\alpha$
(X ₁) DES concentration [%, w/w]	4	8	14	20	24
(X ₂) HBA:HBD molar ratio	1:1	1:2	1:3	1:4	1:5
(X ₃) time of immersion [s]	3.2	10	20	30	36.8

508 ^{a)} k – number of variables = 3

509 In order to identify the most important effects and interactions, analysis of variance (ANOVA)
510 was used. The results of ANOVA tests are presented in Table S3-S4. In the studies, values of
511 typical parameters i.e. F- and p-values were adopted as the criteria at a 95% confidence level. The
512 ANOVA results for both model and real crude oil indicate that in the linear parameters, the effects
513 of the prominent variables are significant on response, with p-values < 0.05. Similar results were
514 obtained in the quadratic parameters. Only for $X_3 \cdot X_3$ the p-value was higher than 0.05. The
515 obtained response levels of the interactions of independent variables indicate that in both types of

516 samples, the relationship between DES concentration and HBA:HBD molar ratio had the greatest
517 impact on the model (p-value < 0.05). In addition, the p-value of both models was found to be
518 statistically significant due to the p-value <0.0001, and F-values equal to 49.58 and 45.55 for real
519 and model crude oil samples respectively. The lack of fit relative to the pure error was considered
520 insignificant due to the p-value of 0.121 and 0.101 for real and model crude oil, respectively.

521 The obtained experimental response equations results of real and model crude oil can be expressed
522 as follow (Eq. 6-7):

523 Real crude oil: $Y_{QR} [g/g] = -101.1 + 32.24 X_1 + 5.15 X_2 + 0.678 X_3 - 1,762 X_1 \cdot X_1 - 0,0999 X_2 \cdot X_2$
524 $- 0,001221 X_3 \cdot X_3 - 0,811 X_1 \cdot X_2 - 0,0561 X_1 \cdot X_3 + 0,01234 X_2 \cdot X_3$ (6)

525 Model crude oil: $Y_{QM} [g/g] = -120 + 36.6 X_1 + 5.91 X_2 + 0.851 X_3 - 1.897 X_1 \cdot X_1 - 0.1079 X_2 \cdot X_2$
526 $- 0.001700 X_3 \cdot X_3 - 0.932 X_1 \cdot X_2 - 0.0693 X_1 \cdot X_3 + 0.01176 X_2 \cdot X_3$ (7)

527 where: Y_{QR} and Y_{QM} - absorption capacity of real and model crude oil;

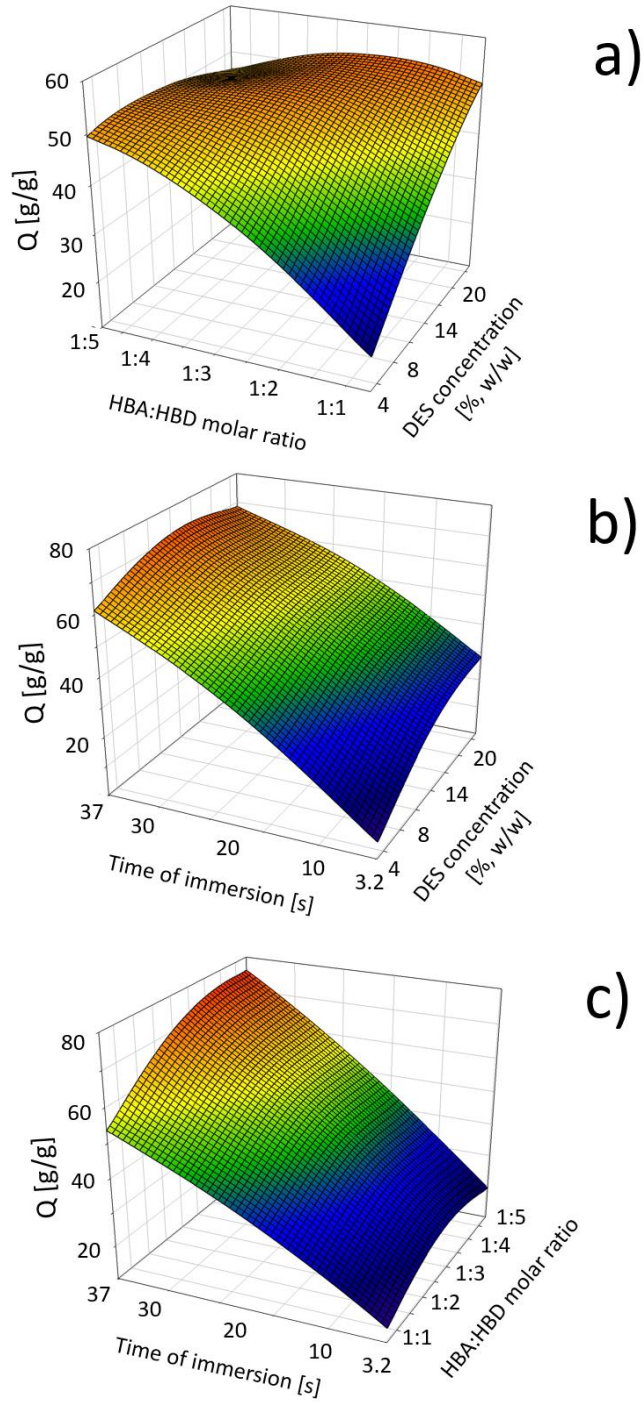
528 X_1 , X_2 , and X_3 - independent variables.

529 In both models high determination (R^2), predicted (R_{pred}^2), and adjusted (R_{adj}^2) coefficients were
530 obtained. For the real crude oil model the following values were obtained $R^2 = 97.81\%$, $R_{pred}^2 =$
531 85.78% , $R_{adj}^2 = 95.84\%$, while for the model crude oil the results were as follows: $R^2 = 97.62\%$,
532 $R_{pred}^2 = 84.48\%$, $R_{adj}^2 = 95.45\%$. The determination coefficient values indicate that in the models
533 there is a good correlation between the experimental results, as well as a good fit of the model and
534 the possibility of predicting the results for new batch data.

535 In both models all parameters i.e. DES concentration (X_1), HBA:HBD molar ratio and time of
536 immersion (X_3) show the significant linear effect on the absorption capacity of real and model

537 crude oil, due to the p-value below 0.05. Furthermore, from the interactive effects of parameters,
538 the DES concentration and HBA:HBD molar ratio is also significant (p-value equal 0.002 for both
539 model and real crude oil models).

540 HBA:HBD molar ratio of impregnated DES is one of the most important parameters which decide
541 to efficient absorption of hydrocarbons phase and low water absorption. Based on Figures 13 and
542 S3 It can be conducted that with the increase of the menthol content in DES structures, the
543 absorption capacity of MS-DES increases. This is probably due to the fact that menthol has –OH
544 group in the structure, which can attract many petroleum compounds containing –CH-, –CH₂- and
545 CH₃ groups, and heteroatoms, i.e. N, S, and O, and for with it strong bonding. Additionally, as
546 observed in point 3.3.5. With the increase in menthol content in DES structures, the WCA
547 increases. This indicates that the MS-E:M (1:5) allows the selective absorption of crude oil from
548 water. DES concentration is also an important parameter that decides the absorption capacity of
549 MS. Too high a concentration of the impregnating solution and consequently too much-
550 impregnating material may clog the pores and reduce the absorption capacity. In addition, too
551 much DES after extrusion can cause DES to enter the pus and make it impossible to reuse it. On
552 the other hand, too low a concentration of DES may cause uneven distribution on the surface of
553 the sponge and result in a lack of selectivity in the process of absorbing oil from water. The
554 obtained results indicate that 15% of the DES solution is an optimum parameter. Lower and higher
555 DES concentrations provide to reduce the absorption capacity of both model and real crude oil. In
556 addition, it can be observed that the absorption equilibrium was reached after 37 sec of immersion.
557 The shorter time meant that the sponge was unable to absorb the oil into all open pores.



558

559 **Figure 5** Response surface plots for real crude oil (CO_3) surface area dependence on: a)

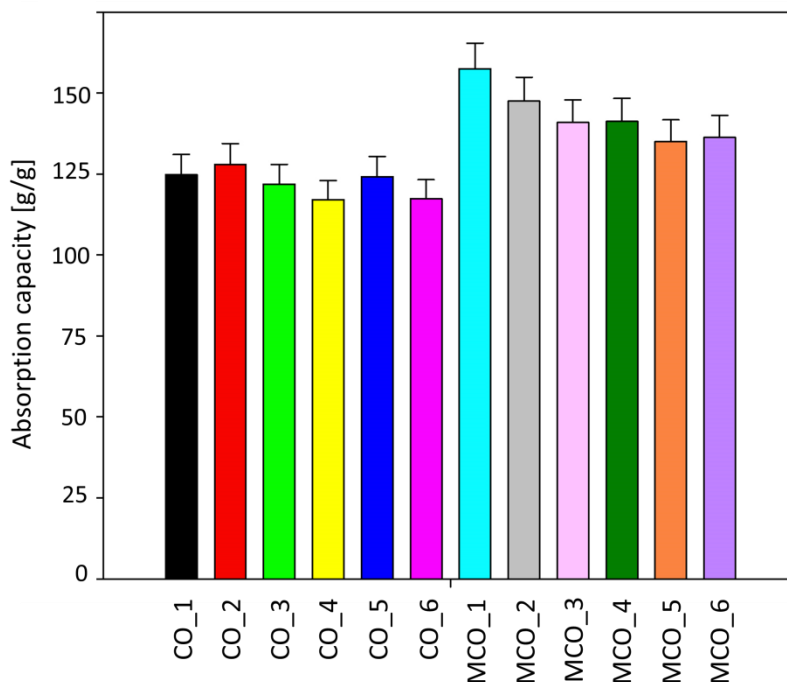
560 HBA:HBD molar ratio and DES concentration, b) time of immersion and DES concentration, c)

561 time of immersion and HBA:HBD molar ratio.

562 3.4.2. Application of MS-DES for absorption of various type of crude oil

563

564 In the further part of the studies, various types of crude oils were absorbed by MS-E:M (1:5) under
565 optimal conditions. The results are presented in Figure 14, and S3. The obtained results indicate
566 that a higher absorption capacity was observed for both relatively light models and real crude oils.
567 The absorption capacity were 99.8, 102.4, 126.1, and 118 g/g for CO_1, CO_2, MCO_1, and
568 M_CO2, respectively. It can be obtained that with the increase in the content of heavier
569 components i.e. resins, and asphaltenes, the MS-E:M (1:5) sorption capacity gradually decreases.
570 This is probably due to the fact that the components with more complex structures have limited
571 access to active sites on the sponge surface, capable of forming strong bonds. In addition, they
572 cover active sites for substances with smaller structures that could more easily attach to the
573 impregnating layer. However, the differences in the absorption capacities of different types of
574 crude oil are very small, so it can be concluded that the sponge can be used with great efficiency
575 to remove different types of crude oil from the water surface. The largest differences in absorption
576 capacities can be observed between the model and real crude oils. In the case of model crude oil,
577 higher absorption capacities were obtained. This is due to the significantly lower amount of
578 substances contained in model mixtures. The same trend has also been observed in other works
579 [61].



580

581 **Figure 6** Absorption capacity of various types of real and mode crude oils using MS-E:M (1:5).

582

583 In order to deep insight into the selected group of crude oils absorption by MS-E:M (1:5), the TLC-

584 FID studies were prepared. Both model and real crude oils groups were analyzed before and after

585 the absorption and squeezing process using the TLC-FID technique (Figure 15 and Table 3). The

586 results indicate that only small differences can be obtained in each crude oil sample before and

587 after the absorption process. The highest differences were observed for real crude oil samples.

588 However, these differences do not excite 2.6 %, w/w which is in the range of error. The results

589 indicate that crude oil after removal from water does not change compositions. In addition, the

590 lack of changes in S, and Ar concentration in crude oil samples indicate that DES does not make

591 it into crude oil. This indicates that the crude oil can be used for further processing and does not

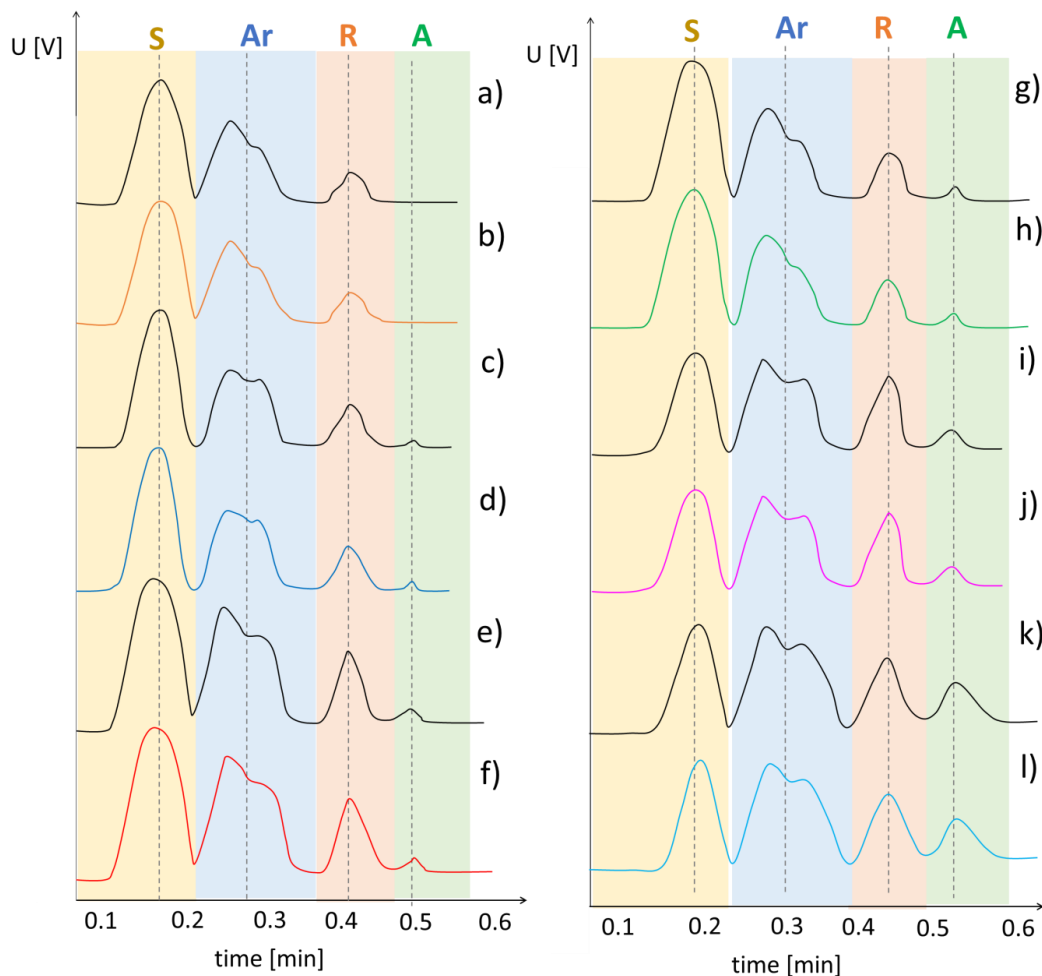
592 need to be disposed of, which has significant financial benefits.

593

594 **Table 2** Composition of the crude oil samples before and after squeezing.

Crude oil sample	S (%, w/w) ± SD		Ar (%, w/w) ± SD		R (%, w/w) ± SD		A (%, w/w) ± SD	
	Pure CO	CO After squeezing	Pure CO	CO After squeezing	Pure CO	CO After squeezing	Pure CO	CO After squeezing
CO_1	70.8 ± 3.7	70.2 ± 3.6	24.2 ± 1.1	23.9 ± 1.2	4.8 ± 0.2	4.9 ± 0.2	0.2 ± 0.01	1 ± 0.05
CO_2	72 ± 4.1	71.6 ± 3.4	22.3 ± 1.1	21.8 ± 1.1	5.0 ± 0.3	5.2 ± 0.3	0.7 ± 0.03	1.4 ± 0.07
CO_3	62.1 ± 3.2	61.2 ± 2.8	19.8 ± 1	19.4 ± 0.9	14.7 ± 0.8	14.8 ± 0.7	3.4 ± 0.2	4.6 ± 0.23
CO_4	72.3 ± 3.8	71.8 ± 3.7	18.2 ± 0.8	18.0 ± 1.0	8.1 ± 0.4	8.5 ± 0.4	1.4 ± 4.3	1.7 ± 0.09
CO_5	39.9 ± 2.2	39.8 ± 2.1	24.9 ± 1	24.6 ± 1.2	30.9 ± 1.7	31.2 ± 1.6	4.3 ± 0.24	4.4 ± 0.22
CO_6	28.1 ± 1.1	28.9 ± 1.6	29.9 ± 1.1	27.9 ± 1.5	32.7 ± 1.8	33.6 ± 1.7	10.2 ± 0.56	7.6 ± 0.39
MCO_1	80 ± 4.4	79.4 ± 3.7	10 ± 0.4	9.8 ± 0.5	9.5 ± 0.5	9.9 ± 0.5	0.5 ± 0.03	0.9 ± 0.05
MCO_2	70 ± 3.4	69.1 ± 2.8	20 ± 1.2	19.9 ± 1	9.5 ± 0.5	10.2 ± 0.5	0.5 ± 0.03	0.8 ± 0.04
MCO_3	50 ± 2.4	49.7 ± 2.4	30 ± 1.2	30.8 ± 1.6	19.5 ± 1.1	19.4 ± 1	0.5 ± 0.03	0.1 ± 0.005
MCO_4	40 ± 1.9	39.2 ± 2.0	50 ± 2.1	50.1 ± 2.6	9.5 ± 0.5	9.9 ± 0.5	0.5 ± 0.03	0.8 ± 0.04
MCO_5	20 ± 1.0	19.3 ± 0.9	40 ± 1.9	41.0 ± 2	38.6 ± 1.8	39.8 ± 2.1	1 ± 0.06	1.3 ± 0.07
MCO_6	10 ± 0.5	9.4 ± 0.5	50 ± 2.1	49.7 ± 2.4	39 ± 2.1	40.7 ± 2.2	1 ± 0.06	0.2 ± 0.01

595



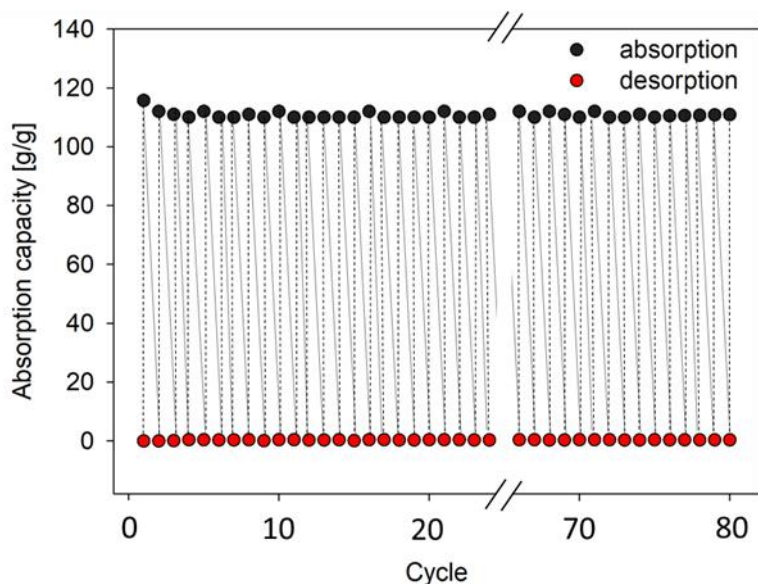
596

597 **Figure 7** TLC-FID chromatograms of real crude oil before (black line) and after absorption and
 598 squeezing process (color lines) a-b) CO_1; c-d) CO_2; e-f) CO_3; g-h) CO_4; i-j) CO_5; k-l)
 599 CO_5.

600 3.4.3. Reusability

601 Reusability is one of the most important parameters that determine the cost of processes. In these
 602 studies, MS-E:M (1:5) was immersed in the real crude oil sample (CO_3) for one minute and then
 603 the sponge was taken out and squeezed in order to remove crude oil. In the next step, the sponge
 604 was dried at 60 °C for 0.5 hours. Sponge after crude oil absorption and after crude oil removal was
 605 weighted. This procedure was repeated 80 times. The obtained results are presented in Figure 16.

606 The obtained results show that the sponges do not change their absorption capacity even after 80
607 cycles.



608
609 **Figure 8** Absorption – desorption reusability cycles of MS-E:M (1:5) for real crude oil sample
610 (CO_3).

611 3.4.4. Comparison of prepared MS-DES with other studies

612 The MS-E:M (1:5) was compared with literature data of other superhydrophobic sponges.
613 However, there are only a few studies of the real crude oil absorption capacity of sponges. Most
614 of the presented works include only results of pure solvents' absorption, which do not relate to very
615 complex crude oil mixtures. A comparison of real crude oil absorption capacity for sponges with
616 different functionalities is presented in Table 4. The results indicate that new MS-DES show higher
617 crude oil absorption capacity than most of the sponges. The water contact angle is comparable to
618 the literature data. Some presented studies required higher surface temperature, which can
619 improved absorption capacity, and selectivity of sponges. However, this increases the energy
620 requirement and thus increases the cost of the entire process. In addition, the possibility of multiple

621 regenerations is a decisive competitive advantage of the new MS in comparison with other
 622 sponges.

623 **Table 4** Comparison of real crude oil absorption capacity for sponges with different functionalities

Type of sponge	Absorption capacity [g/g]	Surface temperature	Water contact angle [°]	Regeneration cycles	Literature
UIO-66-F4@rGO/MS	61	RT	155	10	[62]
MoS2-RS	15-67	76	151	100	[63]
MF/rGO	140.7	92.4	136.8	10	[64]
PDMS/CuS/PDA@MF	117	86.7	169.3	-	[65]
CNT/PDMS-PU	140.7	88	154	-	[66]
TiO ₂ /PDA@MF	11.2	90.7	151	5	[67]
PU	36.3	RT	45	-	[68]
FGN/PU	44.1	RT	160	50	[68]
UMS-3	83.0	RT	131	30	[61]
MS-E:M (1:5)	96.1 – 132.2	RT	152	80	This studies

624

625 4. Conclusions

626 In the studies, a new superhydrophobic and superoleophilic melamine sponges based on deep
 627 eutectic solvents were prepared, characterized, and used for the process of model and real crude
 628 oil removal from water. Due to the fact that the new sponges have to be used in the environmental
 629 waters i.e. sea or ocean, all the tested impregnation layers were composed only of natural
 630 components including terpenes, phenols, and carboxylic acids. The most important parameters that

631 determine the selection of a suitable DES as an impregnating layer were high affinity to the crude
632 oil components and low affinity to water. Based on COSMO-RS preselection, only DES composed
633 of monoterpenes, and linear carboxylic acids met the requirements of suitable impregnation
634 materials. From the wide range of tested melamine sponges impregnated by DES, the MS-E:M
635 (1:5) showed the most favorable properties i.e. superhydrophobic contact angle of 152°,
636 superoleophilic contact angle of 0°, low density of 9.23 mg/cm³, high porosity of 99.39%,
637 relatively high crude oil absorption capacity in the range of 96.1 – 132.2 g/g which only slightly
638 depends on crude oil compositions, excellent reusability which is almost not changing even after
639 80 cycles.

640 The proposed impregnation method with DES, which is cheap, easy, and environmental-
641 friendly, can be used for surface modification of almost all types of new or waste sponges.
642 Therefore, it can be concluded that sponges coated by DES are promising sorbents for crude oil
643 spill containment and environmental remediation.

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649

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