

From polysaccharides to UV-curable biorenewable organo/hydrogels for methylene blue removal

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1 From polysaccharides to UV-curable biorenewable  
2 organo/hydrogels for methylene blue removal

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12 KEYWORDS: UV-curing, polysaccharides, hydrogels

13

14 ABSTRACT

15 Biorenewable “all-starch”-derived organo/hydrogels (OHGs) were prepared *via* “green” and fast  
16 UV-curing and tested as bio-adsorbents for the removal of methylene blue from water.  
17 Methacrylated starch (MS) and acrylated starch derivative,  $\gamma$ -cyclodextrin (ACy), were synthesized

18 for use as ~~hydrogel~~ OHG precursors for the photopolymerization process. Real-time  
19 photorheology confirmed the high reactivity of the prepared photocurable precursors. The  
20 mechanical properties and swelling behaviour of the photocured ~~hydrogels~~ OHGs were examined  
21 focusing on the influence of the increasing amount of ACy. The MS-ACy ~~hydrogels~~ OHGs were  
22 tested as innovative and environmental-friendly biorenewable materials for water treatment, using  
23 methylene blue (MB) as reference pollutant. The experimental data reveal that ~~hydrogels~~ OHGs  
24 containing an increasing amount of ACy show not only superior mechanical strength but also  
25 adsorption properties as a consequence of the high crosslinking efficiency of the acrylated  
26 cyclodextrin derivative and its ability to form host-guest inclusion complexes. Finally, the  
27 printability of these photocurable formulations *via* digital light processing (DLP) 3D – Printing is  
28 confirmed, ~~envisaging which allows to foresee~~ the fabrication of ~~new absorption~~ absorbing  
29 materials with complex ~~but designed geometries for a specific application~~ and application-tailored  
30 ~~geometry, which could represent a new frontier~~ and as such offers new perspectives for wastewater  
31 treatment.

32

## 33 1. INTRODUCTION

34 Water is the most valuable resource for mankind and water pollution caused by human  
35 activities is without question a major environmental problem. Among all aquatic pollutants, dyes  
36 take an ever-growing part and currently their world-wide annual production has reached  
37 approximately 800,000 tons whereby about 10-15% is lost into the environment during their  
38 industrial production [1]. Many dyes are commonly used in various large-scale industrial  
39 commodities such as in textiles, leather, food, paper printing, pharmaceuticals and cosmetics

40 [2,3]. Specifically, textile industry remains the major source of dye-release into the environment  
41 due to the considerable amount of water involved in the dyeing process [4]. As an example, 100  
42 L of water is required to process 1 kg of textiles in traditional textile finishing processes [5]. The  
43 presence of coloured effluents inhibits the growth of the aquatic flora since they limit the  
44 sunlight penetration into waters, thus hindering photosynthesis and reducing the gas solubility in  
45 water [6]. Moreover, most synthetic dyes can cause hazards to humans due to their intrinsic  
46 toxicity. Among commercial dyes, 3,7-bis(dimethylamino) phenazathionium chloride,  
47 commonly known as methylene blue (MB), is one of the most used ones. Since it may provoke  
48 vomit, gastritis, cyanosis, heartbeat increase, jaundice, and tissue necrosis [7,8], its discharge  
49 even in traces into wastewater needs to be minimized.

50 Different processes are currently available for the removal of dye residues from water, such as  
51 chemical oxidation, adsorption, precipitation, membrane-filtration, electrolysis,  
52 photodegradation, electrokinetic coagulation, flocculation with  $\text{Fe(II)/Ca(OH)}_2$ , and also  
53 biological, microbiological, and physiochemical methods [9]. Despite that, many of the existing  
54 approaches have limitations associated to both the production of hazardous by-products and high  
55 energy costs. Among them, adsorption processes are extensively used since they are simple and  
56 cost-effective. Evidently, the adsorption efficiency largely relies on the type of adsorbent.  
57 Activated carbon, mesoporous silica, and magnetic nanoparticles are the most commonly used  
58 materials due to their high adsorption capacity and availability [10-12]. With the aim to develop  
59 low-cost adsorbent materials, several studies have been carried out to evaluate the adsorption  
60 properties of new polymeric hydrogels [13].

61 Hydrogels (HS) are three-dimensional hydrophilic crosslinked polymer networks able to  
62 absorb large quantities of water without dissolving. Therefore, they are gaining increasing

63 attention as adsorbents also for wastewater treatment. However, HS are commonly made of  
64 petroleum-based and non-degradable polymers, generating so-called secondary environmental  
65 pollution [14,15]. This is the reason why in the last years special attention has been given to  
66 adsorbents which are based naturally occurring resources, e.g. carbohydrate-based HS. These are  
67 environmentally friendly, renewable, biodegradable and non-toxic [16,17]. Several  
68 polysaccharides like cellulose [18], chitosan [19,20], starch [21], alginate [22], and dextran [23]  
69 were recently proposed for preparation of low-cost hydrogels [16,24]. Presently, these types of  
70 materials display low mechanical properties which hinder their applicability. Different strategies  
71 can be applied to overcome this problem, like the creation of double-crosslinked networks or the  
72 formation of hybrid hydrogels based on the combination of inorganic and organic materials  
73 [24,25].

74 Starch, in particular, is one of the most abundantly available polysaccharides. It consists of a  
75 mixture of two glucose-derived polymers, namely amylose (linear) and amylopectin (branched),  
76 joined together by  $\alpha(1-4)$  linkages. Moreover, the high availability of hydroxyl groups makes it a  
77 very versatile biopolymer, giving the opportunity of chemical modifications *via* -OH substitution  
78 to prepare a large number of derivatives. And indeed, grafted starch has been previously used for  
79 the removal of metal [26,27] and dye pollutants from water [25].

80 Among starch derivatives, cyclodextrins (CDs), have been proposed as especially interesting  
81 absorbents. CDs are cyclic oligoamyloses, which can be sustainably derived from starch using  
82 glycosyltransferase and consist of either 6 ( $\alpha$ ), 7 ( $\beta$ ) or 8 ( $\gamma$ ) glucose subunits [28,29]. Taking  
83 advantage of their torus-shaped structure, they can be used to trap different pollutants *via* the  
84 generation of the so-called host-guest inclusion complexes [30,31]. Generally, different  
85 crosslinkers and grafting agents are used along with CDs to prepare grafted polymers or

86 copolymers. One of the first CD-based polymers being used for water purification consisted of  
87 CDs crosslinked with epichlorohydrin (ECH) [31-33]. Subsequently, various types of molecular  
88 architectures were developed by simply substituting the hydroxyl moieties of CDs with other  
89 functional groups, to make them suitable for different types of reaction with other polymers [33-  
90 37]. In particular, bio-based hydrogels prepared by using the CDs along with other natural  
91 polymers have shown promising potential in wastewater treatment [38,39]. However, the vast  
92 majority of investigations on hydrogels containing CDs focused on chitosan-based systems [40-  
93 43], while investigations combining CDs with other polysaccharides such as cellulose, starch,  
94 alginate and cotton are still scarce [37,44].

95 So far only few reports mentioned the use of bio-based photo-crosslinked hydrogels for  
96 wastewater treatment [45-47] and only one utilized photo-crosslinked polysaccharides [48].  
97 Photopolymerizations have several advantages over other conventional techniques used to  
98 prepare chemically crosslinked hydrogels, namely fast reaction rates, no volatile organic  
99 compound (VOC) emissions, and no need of heat but comparatively low energy consumption  
100 [49-51].

101 We therefore synthesized new UV-curable polysaccharide-based organo/hydrogels (OHGs)  
102 from starch and  $\gamma$ -cyclodextrin. For this purpose, starch was methacrylated (methacrylated  
103 starch, MS) and  $\gamma$ -cyclodextrin acrylated (acrylated  $\gamma$ -cyclodextrin, ACy) according to previously  
104 reported procedures [51,52]. This procedure makes these molecules suitable for  
105 photopolymerization processes. The aim was to obtain a randomly oriented double network upon  
106 UV-light irradiation of the functionalized polysaccharides. Besides the function as absorbents,  
107 ACys could potentially reinforce the hydrogel-OHG networks, due to the expected and already  
108 proven high crosslinking efficiency [52].

109 The curing kinetics of the photocurable formulations were evaluated *via* real-time photo-  
110 rheology. The mechanical properties and the swelling capability of the photocured **hydrogels**  
111 **OHGs** were investigated with the particular aim to characterize the structure of the crosslinked  
112 networks. Finally, the adsorption properties were investigated in detail to prove the potential  
113 application as bio-based absorbent material for waste-water treatment. Methylene blue (MB) was  
114 used as a model molecule for cationic dyes. Both the capacity and the kinetics of absorption of  
115 the MS-ACy **hydrogels** **OHGs** were investigated. Finally, the printability *via* digital light  
116 processing (DLP) 3D – Printing was demonstrated, envisaging a new frontier for wastewater  
117 treatment through fabrication of complex application-tailored geometries with increased surface  
118 area which may have a profound positive impact on the development of better performing  
119 absorption materials in general [53].

## 120 2. EXPERIMENTAL SECTION

### 121 2.1 Materials.

122 High amylose Hylon VII maize starch (70% amylose) was obtained from Ingredion (Goole, UK).  
123  $\gamma$ -Cyclodextrin was obtained from ABCR. Methacrylic anhydride (MA), triethylamine (>99%)  
124 (TEA), dimethyl sulfoxide (DMSO) (ACS reagent P99.9%), ethanol absolute, acryloyl chloride,  
125 anhydrous n-methyl-pyrrolidone (NMP), methylene blue (MB), **methyl red** and phenylbis(2,4,6-  
126 trimethylbenzoyl)phosphine oxide (BAPO) were purchased from Sigma Aldrich and used  
127 without further purification.

### 128 2.2 Synthesis of methacrylate starch (MS)

129 Methacrylated starch (MS) was synthesized as previously reported [51]. Accordingly, 6 g of  
130 high amylose maize starch were dispersed in 200 mL of DMSO. Subsequently the solution was  
131 heated up at 70°C for 30 min to gelatinize the starch. Then, the solution was cooled down at  
132 room temperature (RT) and 12 mL of MA and 0.22 mL of TEA were added dropwise. The  
133 reaction was left to stir at RT for 18 hours. The products were then precipitated in ethanol,  
134 dissolved in deionized water and precipitate again in ethanol. This procedure was repeated two  
135 times in order to purify the product (47%). The final aqueous solution was lyophilized.

### 136 2.3 Synthesis of acrylated $\gamma$ -cyclodextrin (ACy)

137 Acrylated  $\gamma$ -cyclodextrin (ACy) was prepared as previously reported [52]. Accordingly,  $\gamma$ -  
138 cyclodextrin (20 g) was first dried under high vacuum before being dissolved in anhydrous n-  
139 methyl-pyrrolidone (NMP, 160 mL). Then, the temperature was decreased to 0 °C and acryloyl  
140 chloride (36.07 mL) was added dropwise. The reaction mixture was magnetically stirred at RT  
141 for 72 h at 300 rpm. Dropping the reaction mixture into 2 L of deionized H<sub>2</sub>O gave ACy as a  
142 precipitate (67%). After decanting at RT for 30 min., the product was filtered and washed four  
143 times using deionized H<sub>2</sub>O, before being dried under high vacuum for 24 h.

### 144 2.4 Organo/hydrogel preparation

145 Different photocurable formulations were prepared by dissolving the functionalized  
146 polysaccharide precursors in a H<sub>2</sub>O/DMSO (20/80) mixture. The MS-ACy weight ratio was  
147 varied, while the total monomer concentration was kept at 10 wt% (Table 1). BAPO [1 phr,  
148 (weight per hundred resin)] was used as a photoinitiator. The hydrogels-OHGs were prepared by  
149 pouring the precursor formulations into a silicon mold and irradiating for 1 minute with UV light



150 (100 mW/cm<sup>2</sup>) using a Hamamatsu LC8 lamp equipped with 8 mm light guide (240 to 400 nm as  
151 spectral distribution).

152 **Table 1.** Photocurable formulations.

Sample name	Methacrylated Starch (MS) (wt%)	Acrylated $\gamma$ -Cyclodextrin (ACy) (wt%)	BAPO (phr)
MS	100	0	1
MS-ACy 3-1	75	25	
MS-ACy 2-1	66	34	
MS-ACy 1-1	50	50	
MS-ACy 1-2	34	66	
ACy	0	100	

153

154 2.5 Characterization

155 2.5.1 Nuclear Magnetic Resonance (NMR)

156 <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded on a Bruker Avance 400 Fourier Transform  
157 NMR spectrometer (FT NMR, Bruker, Billerica, MA, USA). The chemical shifts ( $\delta$ ) were  
158 measured and are given in parts per million (ppm) relative to TMS for <sup>1</sup>H NMR and <sup>13</sup>C{<sup>1</sup>H}  
159 NMR, respectively, according to IUPAC. All the spectra were recorded at RT except for the <sup>13</sup>C-  
160 NMR spectra of starch and methacrylated starch which were measured at 60°C to improve the  
161 spectra resolution.

162 2.5.2 Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR)

163 FTIR spectra were recorded by using a Perkin Elmer Spectrum 2000 FTIR spectrometer (Perkin  
164 Elmer, Norwalk, CT, USA) equipped with a single reflection attenuated total reflectance (ATR)  
165 accessory (golden gate). 32 scans were recorded for each sample from 4000 to 500 cm<sup>-1</sup> with a  
166 resolution of 4 cm<sup>-1</sup>.

### 167 2.5.3 Photorheology and Rheology

168 The rheology tests were performed using Anton PAAR Modular Compact Rheometer (Physica  
169 MCR 302, Graz, Austria) in a parallel plate configuration with a quartz bottom glass (25 mm).  
170 The experiments were recorded at RT setting the gap between the plates at 300  $\mu\text{m}$ . Preliminary  
171 amplitude sweep measurements were conducted to define the linear viscoelastic region (LVR) of  
172 the liquid formulations. Real-time photorheology measurements were carried out to evaluate the  
173 curing kinetic of the precursor formulations. The curing process was evaluated by following the  
174 changes in the elastic storage modulus  $G'$  during UV-light irradiation (Hamamatsu LC8 lamp, 30  
175  $\text{mW}/\text{cm}^2$ ). The tests were performed in the LVR setting a constant strain amplitude of 0.5% and  
176 constant frequency ( $\omega$ ) of 6 rad/s. The light was switched on after 30 s to let the system stabilize  
177 before the onset of polymerization. Frequency sweep experiments [ $\omega$ : 0.1–100 rad/s] were then  
178 conducted on freshly crosslinked hydrogels under constant strain amplitude (1%). Finally, the  
179 main structural parameters of the crosslinked hydrogels were calculated as follows. The molar  
180 mass between two entanglement points ( $M_e^*$ ), the ~~crosslinking density~~ numbers of crosslinks ( $\nu_e$ )  
181 and distance between two entanglement points ( $\xi$ ) were obtained from equations 1, 2, and 3,  
182 respectively.

$$183 \quad M_e^* = \frac{cRT}{G_p'} \quad (1)$$

$$184 \quad \nu_e = \frac{G_p' N_A}{RT} \quad (2)$$

$$185 \quad \xi = \frac{1}{\sqrt[3]{\nu_e}} \quad (3)$$

186 Where  $c$  is the concentration,  $R$  is the universal gas constant,  $T$  is the temperature in Kelvin,  
187  $G'_p$  is the storage modulus in the frequency independent plateau region and  $N_A$  is the Avogadro's  
188 number [54].

#### 189 2.5.4 Compression Test

190 Unconfined uniaxial compression tests were performed with a MTS QTest™/10 Elite controller  
191 using TestWorks® 4 software (MTS Systems Corporation, Eden Prairie, Minnesota, USA). The  
192 measurements were performed at RT on cylindrical samples ( $\varnothing=10$ ,  $h=10$ ) with a cell load of 10  
193 N and a head-speed of 0.5 mm/min. The data acquisition rate was set at 20 Hz. The compressive  
194 modulus was estimated as the slope of the linear region of the resulting stress–strain curves.

#### 195 2.5.5 Differential Scanning Calorimetry (DSC)

196 Differential scanning calorimetric analyses were carried out using a Mettler Toledo DSC  
197 instrument. The measures were performed under nitrogen atmosphere (50  $\mu\text{L}/\text{min}$ ) setting a  
198 heating rate of 10  $^\circ\text{C}/\text{min}$ . Approximately 6 mg of each sample were sealed in a 100  $\mu\text{L}$   
199 aluminium pan with pierced lids.

#### 200 2.5.6 Swelling Behaviour

201 The swelling behaviour was investigated by means of gravimetric analysis. The dried hydrogels  
202 OHGs (air drying) were first immersed in deionized water at RT. Then, the samples were  
203 removed from water at different time-intervals and subsequently weighted after removing the  
204 free water present on the surface with a filter paper. The swelling degree (SD%), the equilibrium  
205 swelling ratio ( $S_{eq}$ ) and the equilibrium water content (EWC) were calculated with the following  
206 Equations (4,5,6).

207  $SD\% = \left( \frac{W_t - W_d}{W_d} \right) * 100,$  (4)

208  $S_{eq} = \frac{W_e - W_d}{W_d}$  (5)

209  $EWC\% = \frac{W_e - W_d}{W_e} * 100,$  (6)

210 where  $W_f$   $W_t$  is the ~~final~~ weight at time t,  $W_d$  is the weight of the dry sample, and  $W_e$  is the  
211 weight of the sample at the equilibrium state.

### 212 2.5.7 Field Emission Scanning Electron Microscopy (FESEM)

213 The morphological characterization of the ~~hydrogels~~ **OHGs** was performed by using a FESEM  
214 Zeiss Supra 40 (Oberkochen, Germany). The sample were first lyophilized and then immersed in  
215 liquid nitrogen to induce a fragile fracture. Subsequently, the broken specimens were covered  
216 with a 5 nm thick film of Platinum.

### 217 2.5.8 Adsorption study

218 The adsorption study of MB was conducted by adding 8 mL of MB solution (40 mg/L) to 8 mg  
219 of dried ~~hydrogel~~ **OHG** at  $T = 25$  °C. Afterwards the vials were protected from light with an  
220 aluminium foil to avoid photocatalytic degradation of the dye. Then, fixed amount of supernatant  
221 was taken out at different time-intervals to monitor the dye adsorption. The MB concentration  
222 was determined by JENWAY 6850 UV/Vis (Cole-Parmer, Stone, Staffordshire, UK) UV-visible  
223 spectroscopy by following the peak centred at 665 nm. The adsorption capacity at time t ( $q_m$   
224 [mg/g]) and the equilibrium adsorption capacity ( $q_e$  [mg/g]) were calculated according to  
225 Equations 7 and 8, respectively.

$$226 \quad q_m = \frac{(C_0 - C_t) * V}{W} \quad (7)$$

$$227 \quad q_e = \frac{(C_0 - C_e) * V}{W} \quad (8)$$

228 Where  $C_0$  (mg/L) is the initial MB concentration, while  $C_e$  (mg/L) and  $C_t$  (mg/L) are the MB  
 229 concentration at time  $t$  and at equilibrium, respectively.  $V$  (mL) is the volume of MB solution  
 230 and  $W$  (g) is the mass of the dried hydrogel OHG.

231 Two different kinetic models were then used to evaluate the adsorption rate and the potential  
 232 rate controlling step. The kinetic data were analysed by means of pseudo-first order and pseudo-  
 233 second order models [55], using the Lagergren Equations (9 and 10).

$$234 \quad \frac{dq}{dt} = k_1(q_e - q_m) \quad (9)$$

$$235 \quad -\ln\left(\frac{1 - q_m}{q_e}\right) = k_1 t \quad (10)$$

236 where  $k_1$  is the rate constant of pseudo-first order sorption [1/min]. According to this  
 237 approximation, a plot of  $-\ln((1-q)/q_e)$  vs  $t$  gives a straight line with slope  $k_1$ .

238 Equations 11 and 12 report the second-order kinetic rate equation and its integrated formula  
 239 respectively [56].

$$240 \quad \frac{dq}{dt} = k_2(q_e - q)^2 \quad (11)$$

$$241 \quad \frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (12)$$

242 where  $k_2$  is the rate constant of the pseudo second order sorption [ $\text{g}/(\text{mg min})$ ]. According to  
243 this approximation, a plot of  $t/q$  vs  $t$  gives a linear relationship with slope  $1/q_e$  and intercept  
244  $1/k_2q_e^2$ .

### 245 2.5.9 Digital light processing (DLP) 3D-printing

246 The printability of the precursor formulations by means of DLP 3D – Printing was investigated  
247 using an Asiga UV-MAX DLP printer (nominal XY pixel resolution of  $27 \mu\text{m}$ , light emission at  
248  $\lambda=385\text{nm}$ ). Different CAD models were converted into STL files and 3D printed. The layer  
249 thickness and the light intensity were fixed at  $50 \mu\text{m}$  and  $30 \text{mW}/\text{cm}^2$ , while the exposure time  
250 was ~~set at 3~~ ranged between 2.5 and 3 s, depending on the photocurable formulation being used.  
251 The printed objects were post-cured for 3 min using a mercury lamp provided by Robot Factory  
252 (UV-light,  $12 \text{mW}/\text{cm}^2$ ,  $385 \text{nm}$ ).

253

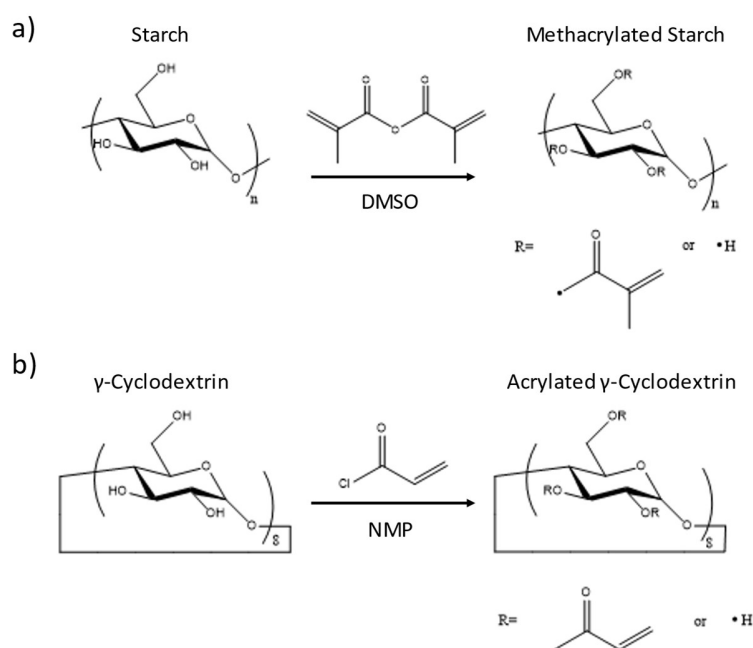
254

255

## 256 3. RESULTS AND DISCUSSION

257 Biorenewable photopolymerized “all-starch” hydrogels OHGs were prepared from  
258 functionalized starch and  $\gamma$ -cyclodextrin, a starch derivative, and tested as bio-adsorbent for the  
259 removal of methylene blue from water. Both of the polysaccharides were functionalized *via*  
260 hydroxyl groups substitution to get derivatives suitable for photopolymerization processes.  
261 Accordingly, methacrylated starch (MS) and acrylated  $\gamma$ -cyclodextrin (ACy) were prepared

262 following two synthetic routes already reported in previous studies, using methacrylic anhydride  
 263 and acryloyl chloride as functionalizing agents (Scheme 1) [51,52]. The complete procedures are  
 264 given in the experimental section.



265

266 **Scheme 1.** Schematic representation of a) starch and b) cyclodextrin functionalization reactions.

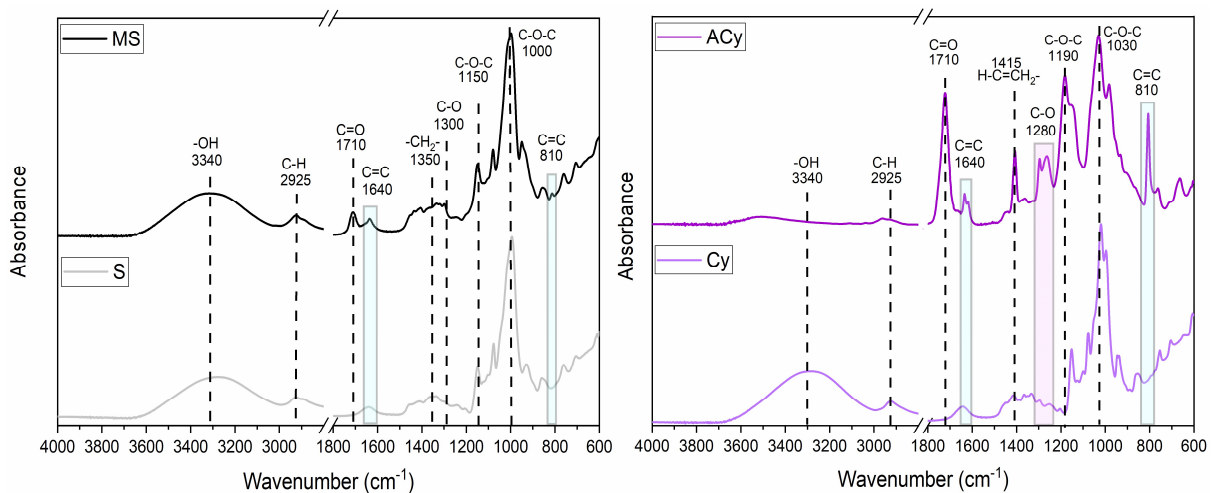
267

268 The successful functionalizations were confirmed by means of  $^1\text{H}$  NMR and  $^{13}\text{C}\{^1\text{H}\}$  NMR,  
 269 which revealed the typical signals of the new vinyl protons ( $\delta^1\text{H}_{\text{MS}} = 5.66$  and  $6.07$  ppm;  $\delta^1\text{H}_{\text{ACy}} = 5.95$ ,  $6.18$ , and  $6.32$  ppm) and carbons ( $\delta^{13}\text{C}_{\text{MS}} = 127.75$  and  $136.61$  ppm;  $\delta^{13}\text{C}_{\text{ACy}} = 128.39$   
 270 and  $132.06$  ppm); methyl protons and carbons ( $\delta^1\text{H}_{\text{MS}} = 1.9$  ppm;  $\delta^{13}\text{C}_{\text{MS}} = 18.45$  ppm) and  
 271 carbonyl carbons ( $\delta^{13}\text{C}_{\text{MS}} = 170.38$  ppm;  $\delta^{13}\text{C}_{\text{ACy}} = 165.57$  ppm) of the photoreactive derivatives  
 272 MS (Fig. S1, Fig. S2) and ACy (Fig. S3, Fig. S4). The obtained degree of substitution (DOS) for  
 273 MS (Fig. S1, Fig. S2) and ACy (Fig. S3, Fig. S4). The obtained degree of substitution (DOS) for

274 the hydroxyl groups were approximately 0.08 for MS and 0.9 for ACy in accordance with what  
275 was reported previously [51,52].

276 The efficiency of the functionalization was further proven by infrared spectroscopy. The ATR-  
277 FTIR spectra of MS and ACy were collected and compared to the spectra of the starting  
278 materials. The detailed assignment of the signals corresponding to the spectral vibrations of both  
279 the main polysaccharides groups and the new chemical functionalities is highlighted in Fig. 1  
280 [57-59].

281 The new characteristic peaks corresponding to the C=CH<sub>2</sub> out of plane bending vibrations and  
282 C=O stretching vibration of meth-/acrylates can be easily observed at 815, 1640 cm<sup>-1</sup> and 1710  
283 cm<sup>-1</sup>, respectively [60-62]. The reduction of the intensity of the signal corresponding to the -OH  
284 vibration at 3340 cm<sup>-1</sup> further confirms the conversion of hydroxyl groups into (meth)acrylated  
285 functions of both starch and  $\gamma$ -cyclodextrin. Note that the reduction of the -OH peak intensity is  
286 more pronounced in the spectrum of acrylated ACy, suggesting confirming a the higher degree  
287 of functionalization [52].



288



289 **Figure 1.** FTIR spectra of pristine Starch (S),  $\gamma$ -cyclodextrin (Cy) and their corresponding  
290 methacrylated derivatives starch (MS) and acrylated  $\gamma$ -cyclodextrin (ACy).

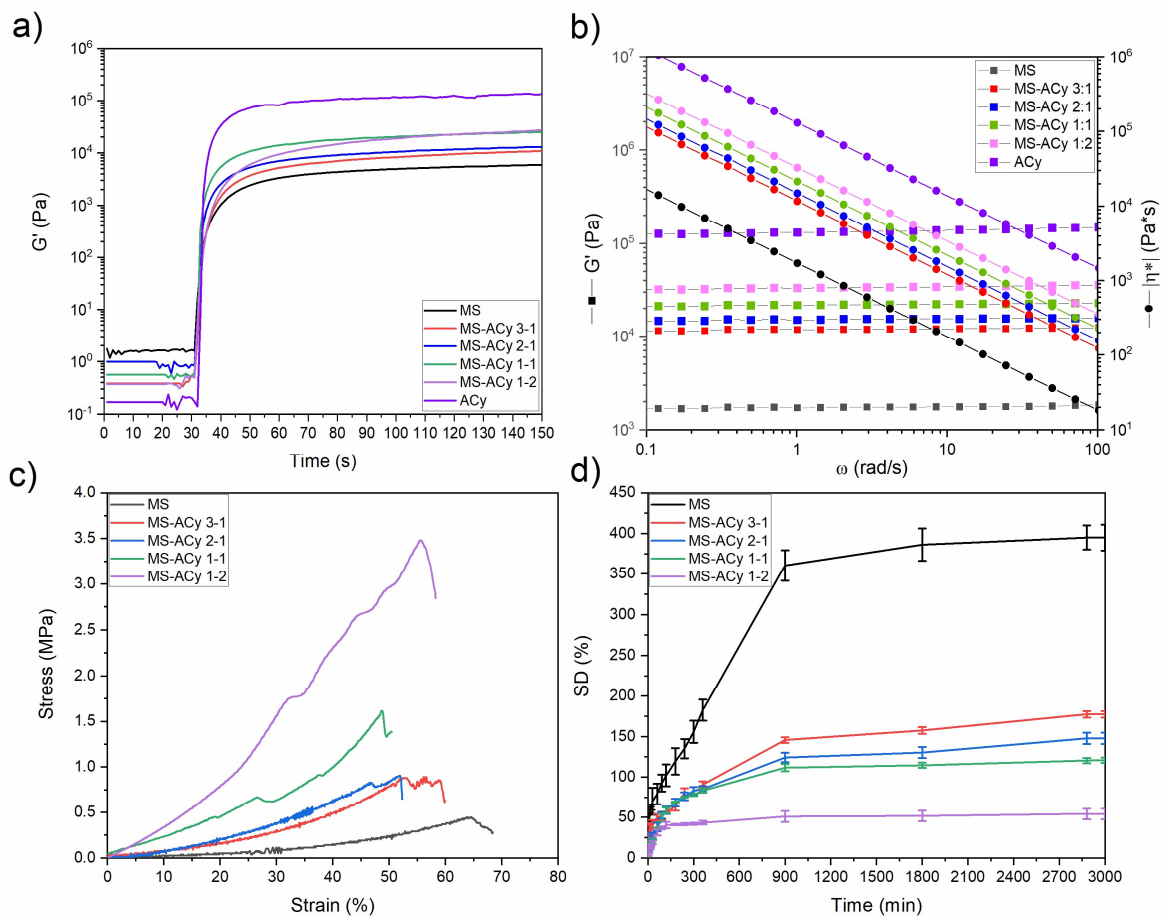
291  
292 Several photocurable formulations were prepared by dissolving different amounts of MS and  
293 ACy in a H<sub>2</sub>O/DMSO (20/80) mixture, while phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide  
294 (BAPO, registered trade name Omnicure 819) was added as a photoinitiator. DMSO was used as  
295 co-solvent in order to increase the solubility of ACy in aqueous formulations. The chemical  
296 composition of the final precursor formulations is given in the experimental section.

297 The photoreactivity of the formulations was evaluated by means of real-time photorheology. The  
298 build-up of the polymer network was monitored by following the storage modulus ( $G'$ ) evolution  
299 during UV-light irradiation. The photorheology curves shown in Figure 2a reveal the high  
300 reactivity of these polysaccharides-based formulations. The induction time, i.e. the minimum time  
301 required to start the photo-induced chemical crosslinking, is less than 2" for all investigated  
302 formulations. Moreover, photo-crosslinking is completed within approximately 60", as confirmed  
303 by the onset of the plateau value of the storage moduli ( $G'$ ). However, even if all formulations  
304 seem to have similar curing kinetics, as suggested by the similar slopes ( $\Delta G'/\Delta t$ ) of the curves, the  
305 reaction rates increase almost three times (from 134 to 335 Pa/s) as the concentration of ACy is  
306 increased in the precursor formulation (see entry 1, Tab. 2). Also, higher  $G'$  values are reached  
307 with increasing ACy content (see entry 2 Tab. 2). This proves that the addition of ACy into the  
308 formulations leads to faster curing kinetics, due to the higher reactivity of acrylates with respect  
309 to methacrylate moieties and the higher degree of functionalization of ACy. The higher  
310 crosslinking efficiency of the cyclodextrin derivatives also generated stiffer hydrogels [52].

311 The viscoelastic properties of the hydrogels-OHGs just formed upon UV-light irradiation were  
312 investigated by means of frequency sweep experiments. The dynamic viscosity  $|\eta^*|$  and the storage  
313 modulus  $G'$  values are reported in Tab. 2. The  $|\eta^*|$  slope values are approximately -0.9 for all the  
314 samples, suggesting a pseudo-plastic behaviour (Fig. 2b) [54]. Furthermore, performing the  
315 analysis in the linear viscoelastic region, it is possible to determine the network parameters in non-  
316 intrusive way, from the  $G'$  measured values [63].

317 The molar mass ( $M_e^*$ ) and the distance ( $\xi$ ) between two entanglements points decreased with  
318 increasing ACy content and the crosslink density ( $\nu_e$ ) increased by more than an order of  
319 magnitude (see entries 3, 4 and 5, Table 2). These results are consistent with the high crosslinking  
320 efficiency of ACy [52]. The influence of ACy on the final properties of the UV-cured  
321 thermosetting networks was further confirmed by the thermo-mechanical characterizations that  
322 were carried out on dried samples. DSC measurements revealed an increase in the glass transition  
323 temperatures ( $T_g$ ) with increasing amount of ACy in the precursor formulations, given that the  
324 increase in the crosslinking density of a polymer reflects into higher  $T_g$  values (Tab. 2) [64].  
325 Furthermore, the mechanical properties of the hydrogels were evaluated by means of compression  
326 tests. The obtained stress-strain curves are shown in Fig. 2c, while the Young's modulus ( $E_c$ ), and  
327 the ultimate compression strength (UCS)-values and compression at break are reported in Tab. 2.  
328 The  $E_c$  values range from 0.78 to 3.93 MPa and are higher than the ones of other polysaccharides-  
329 based hydrogels already reported in the literature [65-67]. Once again, the higher the ACy content,  
330 the higher are both  $E_c$  and UCS, meaning that the presence of ACy improved the mechanical  
331 performance of the photopolymerized networks as a result of the higher  $\nu_e$  values. Whereas the  
332 compression at break slightly decreases in the presence of ACy, as expected for more crosslinked  
333 networks.

334 Subsequently, the water-absorption capability of these polysaccharide-based OHGshydrogels  
 335 was investigated. First, the cured hydrogelsOHGs were immersed in water to remove DMSO *via*  
 336 solvent exchange. Then, the samples were dried and immersed again in water to evaluate the  
 337 degree of swelling at different time-intervals, following the procedure reported in the experimental  
 338 section. The swelling kinetics of the hydrogels-OHGs are shown in Figure 2d and the swelling at  
 339 equilibrium ( $S_{eq}$ ) and the equilibrium water content (EWC) values are listed in Tab. 32. As  
 340 displayed, all the photocured hydrogels-OHGs reach  $S_{eq}$  after approximately 15 hours. However,  
 341 as expected from the crosslinking degree values, the presence of ACy affects the swelling degree,  
 342 since both  $S_{eq}$  and EWC decrease (from 395 to 54 and from 80 to 35, respectively) as the ACy  
 343 content increases.



344

345 **Figure 2.** a) Photorheology curves; b) frequency sweep plots; c) stress-strain curves and d)  
 346 swelling kinetic of the samples prepared from all the precursor formulations.

347

348 **Table 2.** Photo-/rheological, mechanical, thermal and swelling data of the MS-ACy  
 349 organo/hydrogels.

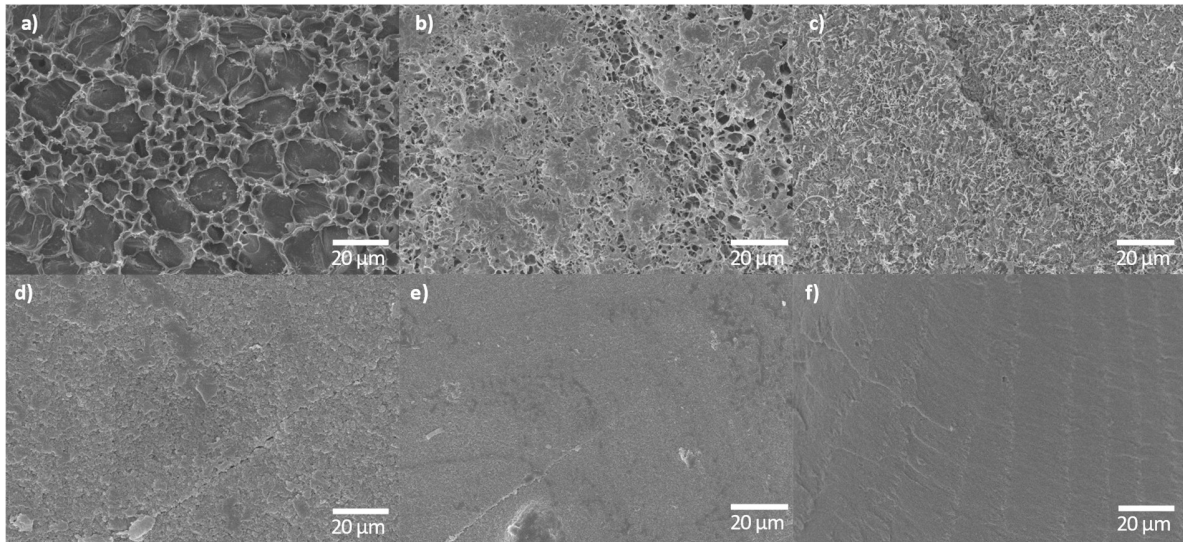
	MS	MS-ACy 3-1	MS-ACy 2-1	MS-ACy 1-1	MS-ACy 1-2	ACy
Reaction rate [Pa/s]	134	201	266	300	335	1800
$G_p^*$ [kPa]	1.8	12.0	15.4	22.1	34.1	131.2
$M_e^*$ [g/Mol]	156.5	22.9	17.9	12.5	8.1	2.1
$v_e$ [1/m <sup>3</sup> ]	$4.3 \cdot 10^{23}$	$2.9 \cdot 10^{24}$	$3.7 \cdot 10^{24}$	$5.4 \cdot 10^{24}$	$8.3 \cdot 10^{24}$	$3.2 \cdot 10^{25}$
$\xi$ [m]	$1.3 \cdot 10^{-8}$	$7.0 \cdot 10^{-9}$	$6.4 \cdot 10^{-9}$	$5.7 \cdot 10^{-9}$	$4.9 \cdot 10^{-9}$	$3.1 \cdot 10^{-9}$
$T_G$ [°C]	95	98	100	102	109	N.A.
$E_C$ [MPa]	0.36±0.15	0.78±0.01	1.04±0.08	2.10±0.28	3.93±0.11	N.A.
Compression at break [%]	64±2.3	56±4.0	52±0.1	49±2.8	56±3.5	N.A.
UCS [MPa]	0.59±0.19	0.89±0.10	0.90±0.13	1.62±0.15	3.48±0.23	N.A.
$S_{EQ}$	3.95±0.15	1.78±0.04	1.47±0.07	1.2±0.03	0.54±0.06	N.A.
EWC [%]	80±0.7	64±0.9	60±1.4	55±1.0	35±2.7	N.A.

350  $M_e^*$  molar mass between two entanglements points,  $\xi$  distance between two entanglements points,  $v_e$  crosslinking  
 351 density numbers of crosslinks,  $E_c$  Young's modulus, UCS ultimate compression strength,  $S_{eq}$  swelling at equilibrium  
 352 and EWC equilibrium water content.

353

354 The effect of ACy on the hydrogel-OHG structure was further proved by the microstructural  
 355 characterization. The FESEM images of the different hydrogels-OHGs are shown in Figure 3  
 356 (higher magnification available in Figure 5S). The structure of the hydrogels-OHGs prepared from  
 357 MS is highly porous, with pore size even higher than 20  $\mu\text{m}$  (Fig. 3a). Instead, the addition of ACy  
 358 in the photocurable formulations leads to a reduction of the porosity. As displayed in Fig. 3b-e,  
 359 both the pore number and size decreased with the increasing ACy content. The microstructure of  
 360 a sample prepared from 100% ACy is given for comparison in Fig. 3f. As you can see, this last  
 361 sample does not present any porosity, at least not in the micrometric scale. These results are in

362 good agreement with the previous findings, further confirming that the addition of ACy leads to  
363 higher crosslinking density (higher  $v_e$ ) with lower  $M_c^*$  and  $\xi$ .



364

365 **Figure 3.** FESEM images of different samples prepared from a) MS, b) MS-ACy 3-1, c) MS-  
366 ACy 2-1, d) MS-ACy 1-1, e) MS-ACy 1-2, f) ACy.

367

368 Finally, the photocured **hydrogels OHGs** were tested as adsorbent materials for the removal of  
369 organic dyes from water. The chelating properties of the hydroxyl groups of starch make these  
370 **hydrogels OHGs** especially promising candidates for the removal of cationic dyes. Moreover, the  
371 presence of cyclodextrins within the structure of the polymeric network can increase the  
372 absorption capability due to the ability of cyclodextrins to form host-guest inclusion complexes.  
373 Methylene blue (MB) was selected as a model dye molecule, due to its fit to the dimension of the  
374 cavity of  $\gamma$ -cyclodextrin that enables efficient complexation [68]. The MB adsorption kinetics are  
375 displayed in Fig. 4.

376 As shown in Fig. 4a, the MB adsorption proceeded rapidly reaching a plateau after about 100  
377 min ( $q_e$ ). The obtained  $q_e$  values are in good agreement with the ones reported in the literature for  
378 other polysaccharides-based hydrogels, such as those prepared with carboxymethyl  
379 cellulose/graphene oxide (GO) (59 mg/g) [69], regenerated cellulose/GO [70], corn stalk/organic  
380 montmorillonite composite (49 mg/g) [71] and carbonized lignosulfonate/gelatin (38 mg/g) [72].

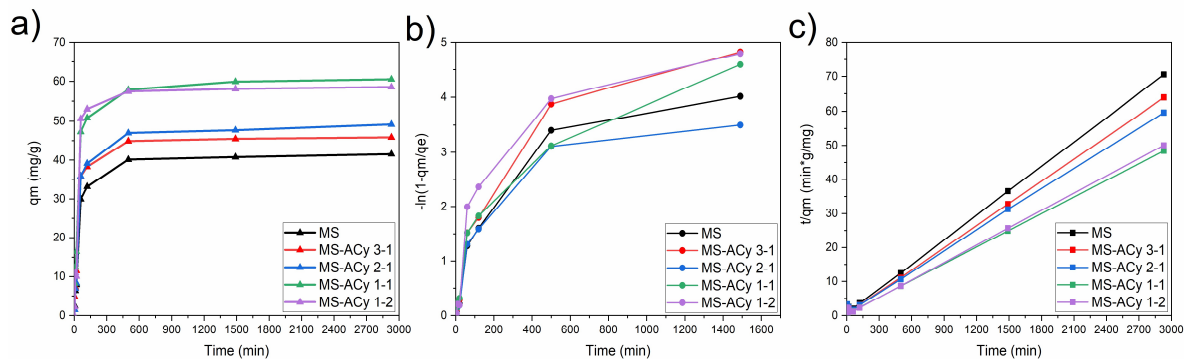
381 The adsorption of cationic dyes into polysaccharides-based hydrogels mainly depends on the  
382 hydrogel composition, since the absorption is mainly affected by the generation of hydrogen  
383 bonds between the hydroxyl groups of the polymer chains and the amide group of the dye  
384 molecule. Moreover, the absorption is also affected by the porosity of the network. Therefore,  
385 the increase of the crosslinking density lowers the free volume and the dye absorption is  
386 expected to decrease accordingly [60].

387 But on the contrary, the relative amount of MB absorbed into our MS-ACy hydrogels-OHGs  
388 increased with the increase of  $v_e$  and the reduction of network porosity. As shown in Table 3, the  
389  $q_e$  of the hydrogels-OHGs increased from 42 to 59 mg/g with increasing content of ACy,  
390 reaching a maximum of +50 wt% with respect to the samples prepared from 100% MS.  
391 However, if the ACy content was furtherly increased the  $q_e$  seems indeed to be negatively  
392 affected. The maximum absorption capability is reached by keeping the ratio MS:ACy at 1:1 and  
393 the 50 wt% of ACy might represent a threshold beyond which the molecular diffusion into the  
394 network is hindered by the  $v_e$  enhancement, resulting into a lower absorption. The higher  
395 absorption values reached with the less porous and more crosslinked hydrogels-OHGs which  
396 show a lowered swelling capability can be explained simply by the increased number of ACy  
397 units which seemingly remain accessible and therefore lead to an increased number of host-guest  
398 inclusion complexes between MB and  $\gamma$ -cyclodextrin [68]. Therefore, the absorption of MB

399 likely occurs following two different mechanisms: a) H-bonding interactions between the  
400 residual -OH groups of MS and ACy and b) MB complexation into the cavity of ACy.

401 The adsorption rates ( $k_a$ ) were also estimated by evaluating the slopes of the first linear part of  
402 the curves [60]. The high  $k_a$  values obtained with an increase from 0.49 to 0.81 [mg/(g\*s)] with  
403 increasing ACy content, (Table 34) suggest that the adsorption mainly occurred on the hydrogel  
404 surface. This finding is consistent with the absorption evolution scaling with time, since the  $q_e$  of  
405 the ~~hydrogels~~ OHGs is reached within the first 100 min, a time much shorter than required to reach  
406 the swelling equilibrium (15 hours).

407 The absorption data were then fitted using pseudo-first-order and pseudo-second-order models.  
408 Fig. 4c-d show the results of the fitting analyses. As can be seen from the graph reported in Fig.  
409 4c, the experimental data do not fit with the linear trend expected from the pseudo-first-order  
410 model which is therefore not applicable ~~the pseudo-first-order model is not applicable, since~~  
411 ~~there is no linear correlation between the experimental and the calculated data~~ [55]. On the  
412 contrary, the pseudo-second-order model correctly describes the MB adsorption into the MS-  
413 ACy ~~hydrogels~~ OHGs, as confirmed by the high correlation coefficient  $R^2$  (>0.99823) and the  
414 calculated absorption capacity ( $q_{e,calc}$ ) values that fit with the experimental data ( $q_{e,exp}$ ). All the  
415 data resulting from the pseudo-second-order fitting are listed in Table 3. The excellent data  
416 fitting with the pseudo-second-order kinetic model suggests that the rate-determining step is  
417 chemisorption [73].



418

419 **Figure 4.** a)  $q_m$  vs time, b) data fitted using the pseudo-first order kinetic model, c) data fitted  
 420 using the pseudo-second-order kinetic model for the absorption of MB into the different MS-ACy  
 421 hydrogels OHGs.

422

**Table 3.** Pseudo-second-order fitting parameters for MB adsorption.

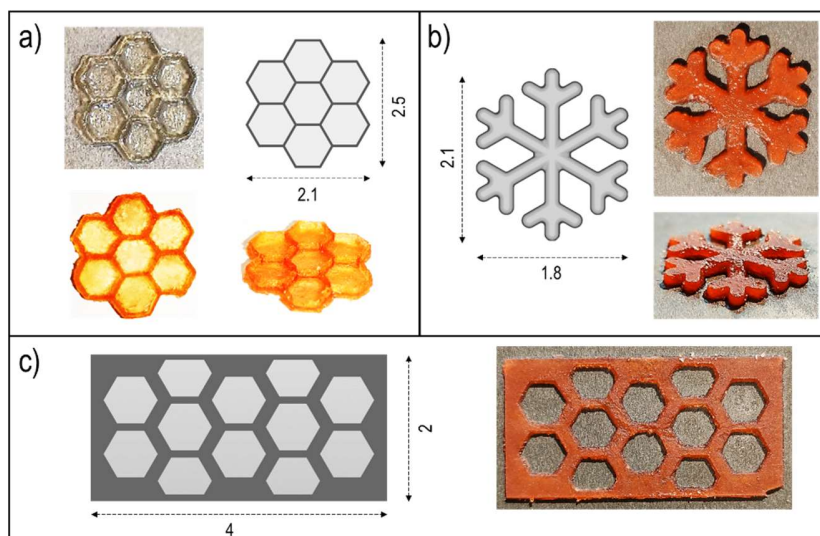
Sample	$k_a$ [mg/(g*s)]	$q_{e, calc}$ [mg/g]	$q_{e, exp}$ [mg/g]	$k_2$ [g/(mg*min)]	$R^2$
MS	0.49	41.52	42.30	$4.52 \cdot 10^{-4}$	0.999525
MS-ACy 3-1	0.58	45.83	46.49	$5.82 \cdot 10^{-4}$	0.999771
MS-ACy 2-1	0.60	49.17	50.40	$2.75 \cdot 10^{-4}$	0.998231
MS-ACy 1-1	0.80	60.53	59.88	$3.08 \cdot 10^{-4}$	0.997972
MS-ACy 1-2	0.81	58.55	61.24	$4.95 \cdot 10^{-4}$	0.996524

423

424 ~~Based on these results of the good reactivity of the investigated formulations towards UV light~~  
 425 ~~initiated photopolymerization, the DLP printability of the most promising formulation with~~  
 426 ~~respect to the absorption capacity was assessed. As shown in Figure 5, free standing 3D printed~~  
 427 ~~geometries were successfully obtained with a good resolution without the use of any additional~~  
 428 ~~dyes during the printing process. This is an interesting preliminary result, as the good DLP-~~  
 429 ~~printability will allow the design of photocured hydrogels with complex geometries to suit specific~~  
 430 ~~applications and to improve the adsorption properties by increasing the surface area of the~~  
 431 ~~hydrogels, which will enhance the process of chemisorption~~



432 Based on the good reactivity of the formulations towards UV-light initiated photopolymerization  
433 (i.e. short induction times and fast curing kinetic), the DLP-printability was assessed, focusing in  
434 particular on the two formulations having the best adsorption properties (MS-ACy 1-1 and MS-  
435 ACy 1-2). First the printability was investigated without using any additional dye. The preliminary  
436 results showed that even though both the formulations can be successfully 3D-printed, the final  
437 resolution of the printed objects was quite low due to over-polymerization (Fig. 5a - top),  
438 especially for those structures having small-scale details (see Fig. S6). Therefore, methyl red (MR)  
439 was added as dye to limit light-diffusion in the vat while printing. The MR concentration was set  
440 at 0.2 phr since this content doesn't affect significantly the photopolymerization kinetic (see Figure  
441 S7) but is enough to improve considerably the printing resolution (Figure 5a - bottom). However,  
442 the structures prepared from MS-ACy 1-1 showed poor self-standing properties. To improve the  
443 mechanical stability, further 3D-printing investigations were carried out by using MS-ACy 1-2,  
444 given that the higher content of ACy leads to more crosslinked and stiffer samples. As shown in  
445 Figure 5b-c, different objects were successfully printed with a good fidelity to the digital CAD  
446 models and a higher mechanical stability. This is an interesting preliminary result, as the good  
447 DLP-printability will allow the design of complex geometries with high surface area would  
448 improve the adsorption properties of the material by enhancing the chemisorption process.



449

450 **Figure 5:** DLP-printed organo/hydrogels from a) MS-ACy 1-1 and b-c) MS-ACy 1-2.

451

452 4. CONCLUSIONS

453 Novel polysaccharide-based photocurable **hydrogels organo/hydrogels** were fabricated *via* UV-  
 454 curing of photoreactive starch and  $\gamma$ -cyclodextrin derivatives and tested as bio-absorbents for the  
 455 removal of methylene blue from water. Methacrylated starch (MS) and acrylated  $\gamma$ -cyclodextrin  
 456 (ACy) were successfully synthesized to be exploited in photocuring processes and the real-time  
 457 photorheology analysis revealed that increasing the ACy content fastens the kinetics due to the  
 458 high reactivity of the multi-acrylated macromer. Rheological, thermo-mechanical and  
 459 morphological tests performed on the photocrosslinked hydrogels revealed that higher amounts  
 460 of ACy lead to an increase of the cross-link density, with the formation of stiffer networks with  
 461 smaller porosity. Besides fastening the photopolymerization kinetic and stiffening the resulting  
 462 **hydrogel**-networks, ACy had a strong influence on the absorption capabilities of the  
 463 **hydrogels OHGs**. The results of the swelling and absorption tests revealed that the final properties

464 of the ~~hydrogels~~ OHGs could be easily tailored by modulating the ingredients within the  
465 precursor formulations. In fact, even if the swelling equilibrium values decreased, higher MB  
466 absorption capacity was recorded with the increase of ACy content ~~into the hydrogel~~, possibly  
467 due to the combination of the chelating properties of the hydroxyl groups of MS and the ability  
468 of ACy to form inclusion complexes with MB. All the ~~HS~~-absorption experimental data correctly  
469 fitted with the pseudo-second-order kinetic model, suggesting chemical adsorption. Furthermore,  
470 the DLP printability of these polysaccharides-based ~~hydrogels~~ OHGs was demonstrated, opening  
471 a new frontier for wastewater treatment.

472

473

474

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479 **Author Contributions**

480 The manuscript was written through contributions of all authors. All authors have given approval  
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485 ABBREVIATIONS

486 S Starch, MS Methacrylated Starch, C  $\gamma$ -Cyclodextrin, AC Acrylated  $\gamma$ -Cyclodextrin.

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