

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, γ -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 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 (α), 7 (β) or 8 (γ) 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 γ -cyclodextrin. For this purpose, starch was methacrylated (methacrylated
103 starch, MS) and γ -cyclodextrin acrylated (acrylated γ -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 γ -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 γ -cyclodextrin (ACy)

137 Acrylated γ -cyclodextrin (ACy) was prepared as previously reported [52]. Accordingly, γ -
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 H₂O 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 H₂O, 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 H₂O/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-OHG were prepared by
149 pouring the precursor formulations into a silicon mold and irradiating for 1 minute with UV light

150 (100 mW/cm²) 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 γ -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 ¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker Avance 400 Fourier Transform
157 NMR spectrometer (FT NMR, Bruker, Billerica, MA, USA). The chemical shifts (δ) were
158 measured and are given in parts per million (ppm) relative to TMS for ¹H NMR and ¹³C{¹H}
159 NMR, respectively, according to IUPAC. All the spectra were recorded at RT except for the ¹³C-
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⁻¹ with a
166 resolution of 4 cm⁻¹.

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 μm . 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 mW/cm^2). The tests were performed in the LVR setting a constant strain amplitude of 0.5% and
176 constant frequency (ω) 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 [ω : 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 (v_e)
181 and distance between two entanglement points (ξ) were obtained from equations 1, 2, and 3,
182 respectively.

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

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

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

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 μL
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 s, ranging 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, $12 \text{mW}/\text{cm}^2$, 385nm).

253

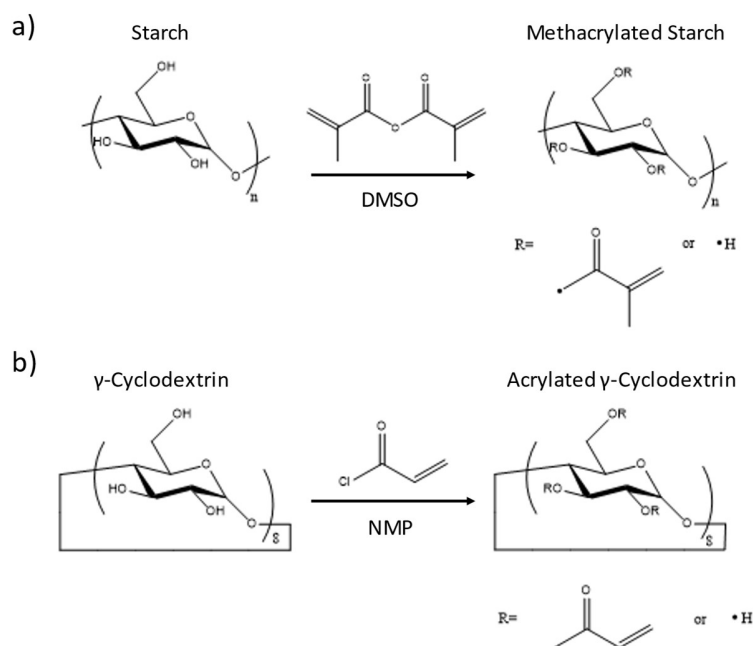
254

255

256 3. RESULTS AND DISCUSSION

257 Biorenewable photopolymerized “all-starch” hydrogels OHGs were prepared from
258 functionalized starch and γ -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 γ -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.

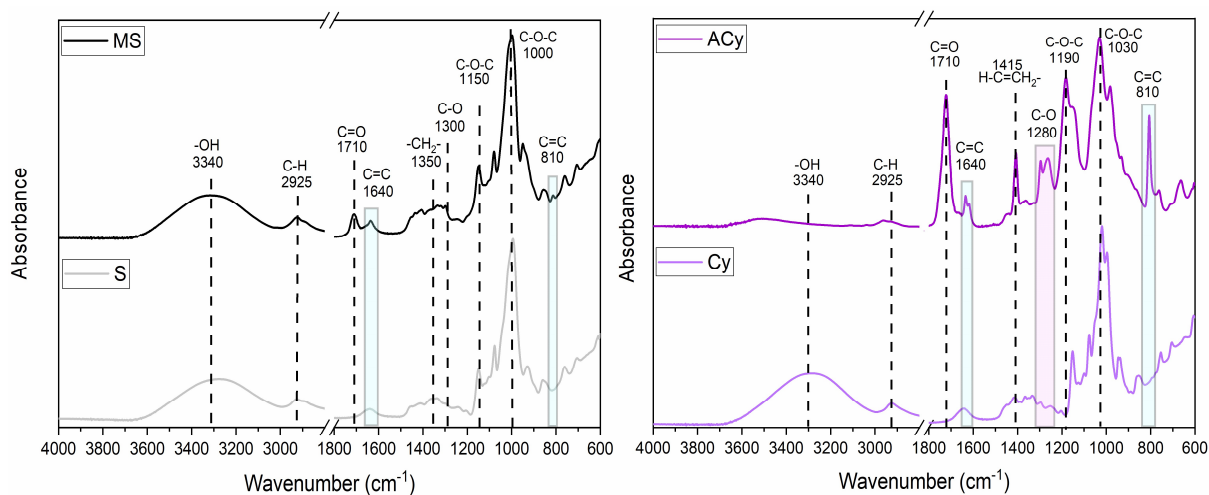
267

268 The successful functionalizations were confirmed by means of ^1H 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=CH₂ out of plane bending vibrations and
282 C=O stretching vibration of meth-/acrylates can be easily observed at 815, 1640 cm⁻¹ and 1710
283 cm⁻¹, respectively [60-62]. The reduction of the intensity of the signal corresponding to the -OH
284 vibration at 3340 cm⁻¹ further confirms the conversion of hydroxyl groups into (meth)acrylated
285 functions of both starch and γ -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), γ -cyclodextrin (Cy) and their corresponding
290 methacrylated derivatives starch (MS) and acrylated γ -cyclodextrin (ACy).

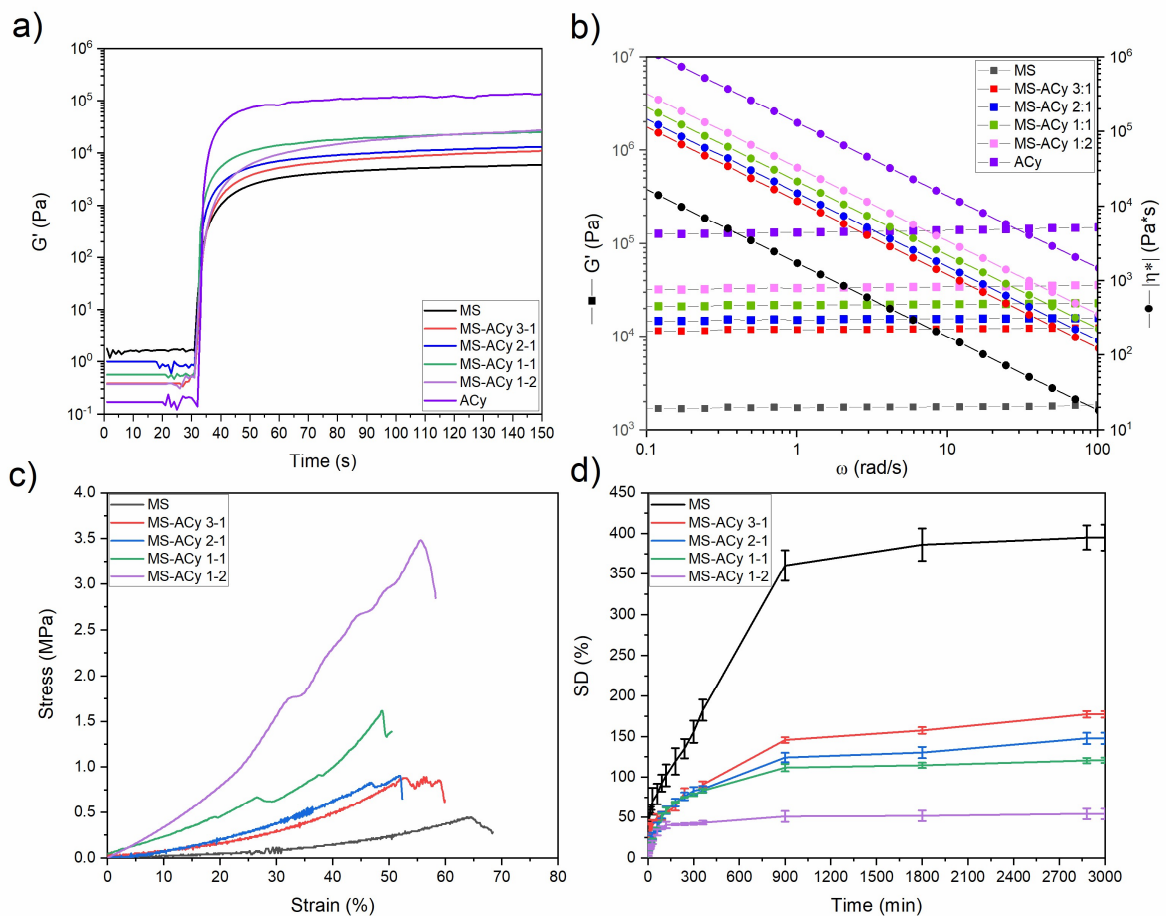
291
292 Several photocurable formulations were prepared by dissolving different amounts of MS and
293 ACy in a H₂O/DMSO (20/80) mixture, while phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide
294 (BAPO, registered trade name Omnicure 819) was added as a photoinitiator. DMSO was used as
295 co-solvent 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 (ξ) between two entanglements points decreased with
318 increasing ACy content and the crosslink density (ν_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 ν_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.

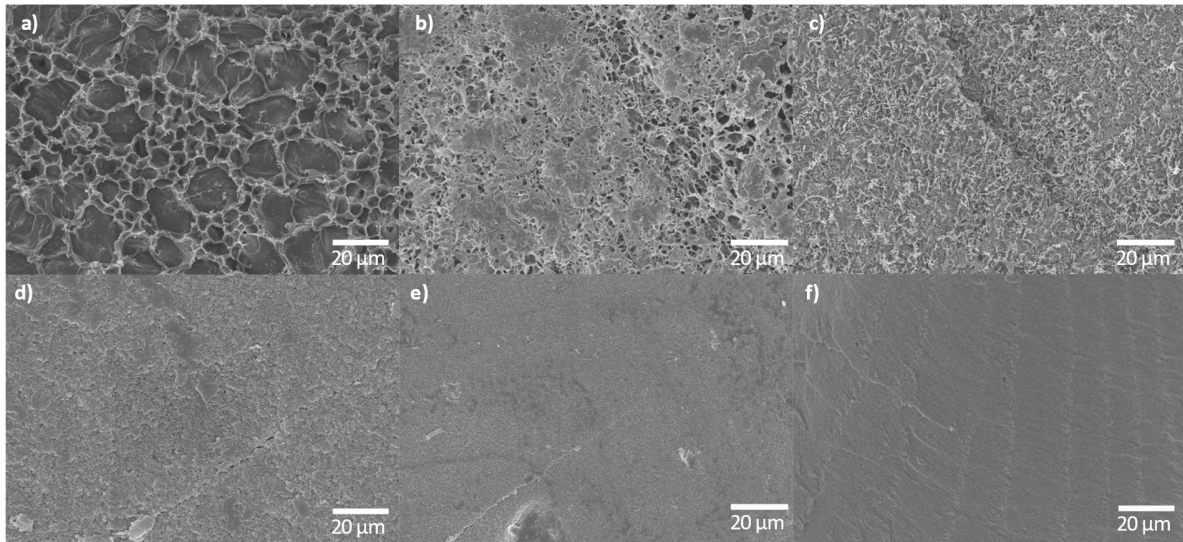
	MS	MS-ACy 3-1	MS-ACy 2-1	MS-ACy 1-1	MS-ACy 1-2	ACy
Reaction rate [Pa/s]	134	201	266	300	335	1800
G_p^* [kPa]	1.8	12.0	15.4	22.1	34.1	131.2
M_e^* [g/Mol]	156.5	22.9	17.9	12.5	8.1	2.1
v_e [1/m ³]	$4.3 \cdot 10^{23}$	$2.9 \cdot 10^{24}$	$3.7 \cdot 10^{24}$	$5.4 \cdot 10^{24}$	$8.3 \cdot 10^{24}$	$3.2 \cdot 10^{25}$
ξ [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, ξ 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 μm (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 ξ .



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 γ -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].

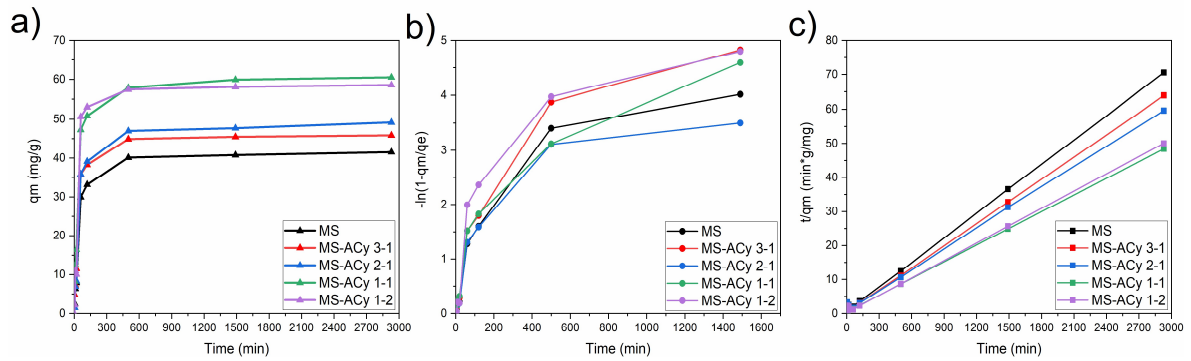
381 The adsorption of cationic dyes into polysaccharides-based hydrogels mainly depends on the
382 hydrogel composition, since the absorption is mainly affected by the generation of hydrogen
383 bonds between the hydroxyl groups of the polymer chains and the amide group of the dye
384 molecule. Moreover, 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-OHG
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-OHG 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-OHG 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 γ -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

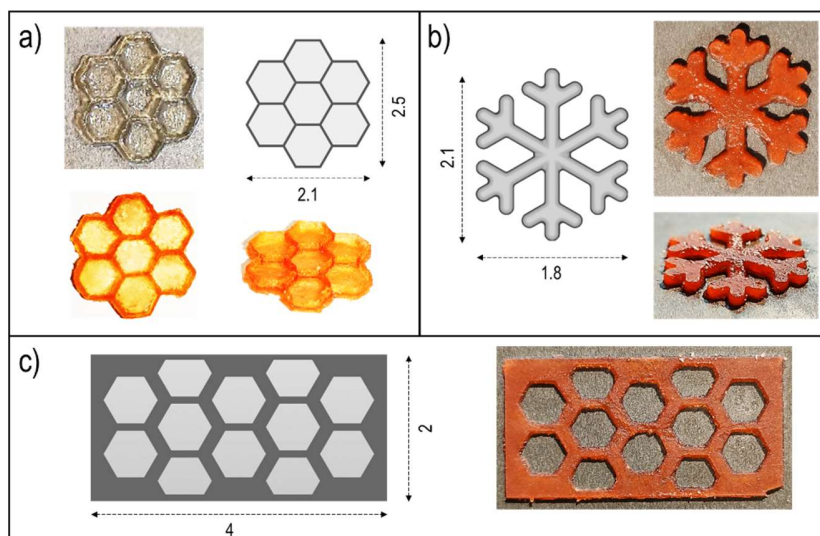
Table 3. Pseudo-second-order fitting parameters for MB adsorption.

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 γ -cyclodextrin derivatives and tested as bio-absorbents for the
 455 removal of methylene blue from water. Methacrylated starch (MS) and acrylated γ -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
481 to the final version of the manuscript.

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485 ABBREVIATIONS

486 S Starch, MS Methacrylated Starch, C γ -Cyclodextrin, AC Acrylated γ -Cyclodextrin.

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