

# Catechol-containing acrylic Poly(ionic liquid) Hydrogels as Bioinspired Filters for Water Decontamination

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**ABSTRACT:** Mussel inspired catechol containing materials have currently drawn great attention as biomaterials, adhesives, surface coating and in bioelectronics, among other

applications. In this work, we mimicked the ability of mussels as water filtration systems to adsorb organic and inorganic contaminants. For this purpose, the synthesis of biomimetic hydrogels was carried out based on the co-polymerization of a new ionic monomer, dopamine methacrylic salt (iDA) with a series of water soluble methacrylate monomers by visible light photopolymerization. The iDA ionic monomer is highly water soluble as compared to previous reported monomers containing catechol groups. This allows its incorporation into different acrylic hydrogels in concentrations up to 50 % mol of monomers containing catechol groups, leading to functional materials with variable morphology and swelling properties. The hydrogels displayed to be highly effective for the removal of heavy metals such as As(V) and Cr(VI) with very good effectiveness compared to other natural sorbents commonly employed, such as clays. Besides, these catechol functional poly(ionic liquid) hydrogels were evaluated in the removal also of other pollutants such as organic dyes with different charge. Preliminarily results demonstrate the versatility of these materials that combine catechol and ionic chemistry for the absorption of a wide variety of water pollutants.

## 1. INTRODUCTION

The catechol functional group is a widely occurring moiety within natural products found in plants and animals. In recent years, polymers containing catechol moieties have been designed, mostly for their bio-adhesion properties.<sup>1,2</sup> The inspiration came from the proteins secreted by mussels which can strongly attach to a wide variety of substrates.<sup>3, 4</sup> Furthermore, the rich chemistry of catechol has expanded the topic of bioinspired materials with applications not only as adhesives but also in the areas of surface functionalization, structural materials, biomaterials or even batteries.<sup>3,5-13</sup> On the other hand, the introduction of new ionic moieties (cations and anions) into polymers is giving rise to a novel family of functional polymers called poly(ionic liquid)s. Poly(ionic liquid)s have expanded the properties and applications of both molecular ionic liquids and common polyelectrolytes. They have become an emerging interdisciplinary topic in polymer chemistry and physics, materials science, catalysis, separation, analytical chemistry or electrochemistry.<sup>14</sup> Interestingly, poly(ionic liquid)s have shown great ability to be used in water purification systems in applications ranging from coatings for micro-extraction of contaminants,<sup>15</sup> water flocculants for water filtration,<sup>16</sup> porous absorbents,<sup>17</sup> anionic dyes absorbers and pH indicators.<sup>18</sup>

In general, pollutants removal's methods are based on chemical oxidation, coagulation, flotation, chemical or biological degradation, among others.<sup>19</sup> However, recent studies have shown that purification techniques currently used are not totally effective for their removal. In this way, new materials have been synthesized to improve removal efficiencies.<sup>20</sup> In particular, adsorption is considered one of the most suitable water treatment methods due to its ease operation procedures and the wide range of adsorbents that can be employed. Thus, the development of new adsorbents with improved properties, such as high adsorption capacity, rapid adsorption speed and mechanically resistant has generated a great interest in the development of new adsorbent materials based on hydrogels.<sup>19</sup>

Besides its excellent adherence to rocks, mussels are recognized as natural water filtration systems, constantly sieving the water for a meal of bacteria or microscopic algae. As they filter water, the tissues of the bivalves absorb chemicals - like herbicides, pharmaceuticals and flame retardants - and pathogens.<sup>21, 22</sup> This inspired us to combine catechol polymer chemistry within new poly(ionic liquid)s as new polymeric materials for water purification. Recently, this combination was proposed by Detrembleur et al. to be used in energy.<sup>23</sup> In this way, we decided to develop a new platform of hydrogels functionalized both by catechol and ionic moieties. At this respect, monomers containing catechol groups, such as dopamine methacrylamide or 4-vinyl catechol, are usually copolymerized in a protected form via a free-radical polymerization with vinyl monomers.<sup>24-26</sup> However, in the case of hydrogels, the incorporation of catechol co-monomers is restricted to less than 20% mol due to the poor water solubility of (co)polymers containing catechol.

To overcome this limitation in the functionalization degree of the hydrogels with catechol groups, in this paper we designed a highly water soluble catechol-containing ionic monomer, dopamine methacrylic salt (iDA). Then, a new family of acrylic hydrogels were synthesized by photo co-polymerization of iDA with acrylic monomers in water solutions employing a vitamin as sensitizer (Riboflavine) and blue leds as irradiation source. We chose this synthetic method because of its green aspects and its low energy requirements and versatility. This paper presents the synthesis and characterization of the catechol poly(ionic liquid) hydrogels with three different co-monomers acrylamide (AAm), [2-(methacryloyloxy) ethyl] trimethylammonium chloride (METAC) and 2-hydroxyethyl acrylate (HEA). We also show some studies of the swelling of the hydrogels depending on the composition. As a potential application, the paper presents promising results of absorption of heavy metals and organic compounds removal using these hydrogels.

## **2. EXPERIMENTAL SECTION**



**2.1 Materials and Methods.** An anionic exchange resin (AER) from Alfa Aesar (Amberlyst A-26 (OH), 0.8 mol L<sup>-1</sup>), commercial methacrylic acid (MA) from Sigma Aldrich and dopamine hydrochloride (DAHCl) from Alfa Aesar were employed for the synthesis of the new ionic monomer.

2-Hydroxyethylacrylate (HEA) (~ 96%), acrylamide (AAm) (~ 99%) and [2-(methacryloyloxy) ethyl] trimethylammonium chloride (METAC, 80% in water) (~ 97%), were obtained from Sigma-Aldrich and used for the synthesis of the hydrogels. Polymerization inhibitors (quinone derivatives) were removed through the passage of liquid monomers through a column containing an exchange resin (De-Hibit-200® from Polyscience Inc.). A functionalized silsesquioxane with amino and methacrylate groups (SFMA) synthesized in our laboratory was employed as co-initiator and cross-linking agent.<sup>27</sup> Riboflavin (Rf, 98%) (Vitamin B2) was obtained from Sigma-Aldrich and was used as a natural sensitizer.

Simulated aquifer solution was prepared with 0.1M of NaCl from Sigma Aldrich with pH 6 (regulated with HCl).

Commercial organic dyes were employed to simulate textile wastes: Eosin Y (~99%) (EoY), Methylene Blue (~99%) (MB) and Safranin (~99%) (Saf), all from Sigma Aldrich. Employed inorganic salts were: CoCl<sub>2</sub> (~99.99%), Cu(NO<sub>3</sub>)<sub>2</sub> (~99.99%), Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O (~98%) from Sigma Aldrich, and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (~98%) from Merck.

The phosphomolibdate method was employed for the colorimetric detection of As(V). Ascorbic acid, sodium tartrate and sodium molibdate, all from Merck, were employed as received for the colorimetric detection of Cr(VI); 1,5-Diphenylcarbazide from Sigma Aldrich was employed as indicator and complexing compound.<sup>28, 29</sup>

**2.2 Synthesis of dopamine methacrylic acid salt (iDA).** The synthesis of iDA was carried out using an anionic exchange resin (AER), (exchange capacity 0.8 mol L<sup>-1</sup>), an excess (>10% w/v) of commercial methacrylic acid, water and 0.05M of dopamine chloride in methanol. The AER column was loaded with an excess of methacrylic acid solution

(>10% w/v). Then, a 0.05M dopamine chloride solution in methanol was passed slowly through the column. The final product, dopamine methacrylate (iDA), was collected in the form of a methanol solution. Methanol was removed under reduced pressure, and the iDA was characterized by FTIR and <sup>1</sup>H-NMR (Figure 1b-c). <sup>1</sup>H-NMR (D<sub>2</sub>O): δ= 1.93 ppm (s, 3H, CH<sub>3</sub>), 2.81 ppm (t, 2H, CH<sub>2</sub>-NH<sub>3</sub>), 3.10 ppm (t, 2H, CH<sub>2</sub>-CH<sub>2</sub>-NH<sub>3</sub>), 5.27 ppm (s, 1H, CH<sub>2</sub>=C), 5.78 ppm (s, 1H, CH<sub>2</sub>=C), 6.72 ppm (m, 3H, aromatic).

**2.3 Synthesis of the ionic hydrogels.** Hydrogels were synthesized by free radical photopolymerization employing aqueous solutions of 50% w/v of the monomers. AAm, HEA and METAC were used to co-polymerize with iDA at various monomer mixture ratios (15%, 30% and 50% mol). SFMA was employed as a cross-linker/co-initiator and Rf as the sensitizer, both at a concentration of 1% w/v in water with respect to the mass of monomers.

4 mL of the de-oxygenated pre-polymeric mixture was irradiated with constant stirring for 3 h at room temperature in a home photoreactor composed of 12 blue light emitting diodes (LEDs) (λ<sup>max</sup> 455 nm). After irradiation, tubes were maintained for 48 h in the dark. Then, hydrogels were removed by breaking the tubes and cutting the cylinders into uniform discs of 10.5 mm in diameter and 2.5 mm in thickness (~0.10 g). They were washed twice with MilliQ water for 5 h to remove any unreacted species and finally dried in an oven at 40°C for 48 h.

All samples were dried before analysis to ensure the absence of water. All assays were carried out by duplicate.

**2.4 Characterizations.** The new synthesized monomer and ionic hydrogels were characterized by proton nuclear magnetic resonance (<sup>1</sup>H-NMR), recorded in a Bruker Avance 400 spectrometer operating at 400.15 MHz. Fourier transform infrared (FTIR) spectra were recorded at room temperature with an Alpha Bruker- IR spectrometer applying 10 scans in transmission mode.

Materials thermal properties were analyzed by differential scanning calorimetry (DSC) performed on a DSC Q2000 differential calorimeter (TA Instruments). All the experiments were performed under ultrapure nitrogen flow. Measurements were performed by placing the samples (~5 mg) in sealed aluminum pans. The samples were heated at a rate of 20 K min<sup>-1</sup>, from - 50 °C to 100 °C.

To visualize the pore structure of the hydrogels in the swollen state, a JEOL JSM-6460 LV SEM (Scanning Electronic Microscopy), from Jeol Technics Ltd., Tokyo, Japan, was employed. The samples were swollen 15 h in simulated aquifer media at 25°C. Before SEM analysis, they were lyophilized to observe pore structure.

**2.5 Swelling assays.** Dry discs of the hydrogels were weighted ( $W_0$ ) and immersed in simulated aquifer at 25°C. At specified times, the samples were removed from the solution, blotted with filter paper to eliminate excess of solution, and weighted ( $W_t$ ). The results were adjusted according to Equation 1.<sup>30,31</sup>

$$S_w = \frac{W_{water}}{W_{pol}} = \frac{(W_t - W_0)}{W_0} = K_p t^{n_p} \quad (1)$$

Where  $K_p$  and  $n_p$  represent the kinetic constant of water diffusion into the network and the swelling exponent, respectively.

**2.6 Pollutant removal procedure.** Organic and inorganic pollutants were employed in a limited concentration established by the World Health Organization.<sup>32</sup> Each pollutant was followed by UV-Vis spectrophotometer from the maximum absorption peak of the substance or from the employment of complexes for colorimetric detection. A calibration curve was built for each species. Measurements were realized at room temperature with a Perkin-Elmer UV/Vis Lambda 950 spectrometer

For contaminants removal, a dried disc of hydrogel was submerged in 10 mL of simulated aquifer with a particular pollutant, thus, at certain consecutive times, 3 mL of the remain solution was analyzed by UV-Vis spectrophotometer, after that, solutions were returned to the original flask. The detection was carried out until 24-48 h. The adsorption

capacity,  $q$  (mg of contaminant adsorbed per kilogram of dry hydrogel) of the polymers was calculated using Equation 2:

$$q = \frac{(C_i - C_t)V}{m} \quad (2)$$

Where  $C_i$  and  $C_t$  represent the initial concentration and the concentration at time  $t$  of the pollutant ( $\text{mg mL}^{-1}$ ), respectively,  $V$  is the total volume of the contaminant solution (mL) (in contact with the hydrogel) and  $m$  is the polymer mass (Kg).

**2.6.1 Kinetic study.** Lagergren model. A kinetic analysis of the pollutants removal was performed employing the differential equation of the pseudo-first-order developed by Lagergren:<sup>33</sup>

$$\frac{dq_e}{dt} = k(q_e - q_t) \quad (3)$$

Where  $q_e$  and  $q_t$  refer to the amount of contaminant adsorbed ( $\text{mg Kg}^{-1}$ ) at equilibrium and a given time ( $t$ , h), respectively, and  $k$  is the rate constant of pseudo-first-order adsorption ( $\text{h}^{-1}$ ). Integrating Equation 4 for the boundary conditions (from  $t=0$  and  $q_t=0$  to  $t$  and  $q_t$ ) gives the equation:

$$\ln\left(\frac{q_e}{q_e - q_t}\right) = k t \quad (4)$$

Which is the integrated rate law for a pseudo-first-order reaction. Rate constant ( $k$ ) can be determined from the slope of the straight-line plots of  $\ln(q_e/(q_e - q_t))$  against  $t$ .

### 3. RESULTS AND DISCUSSION

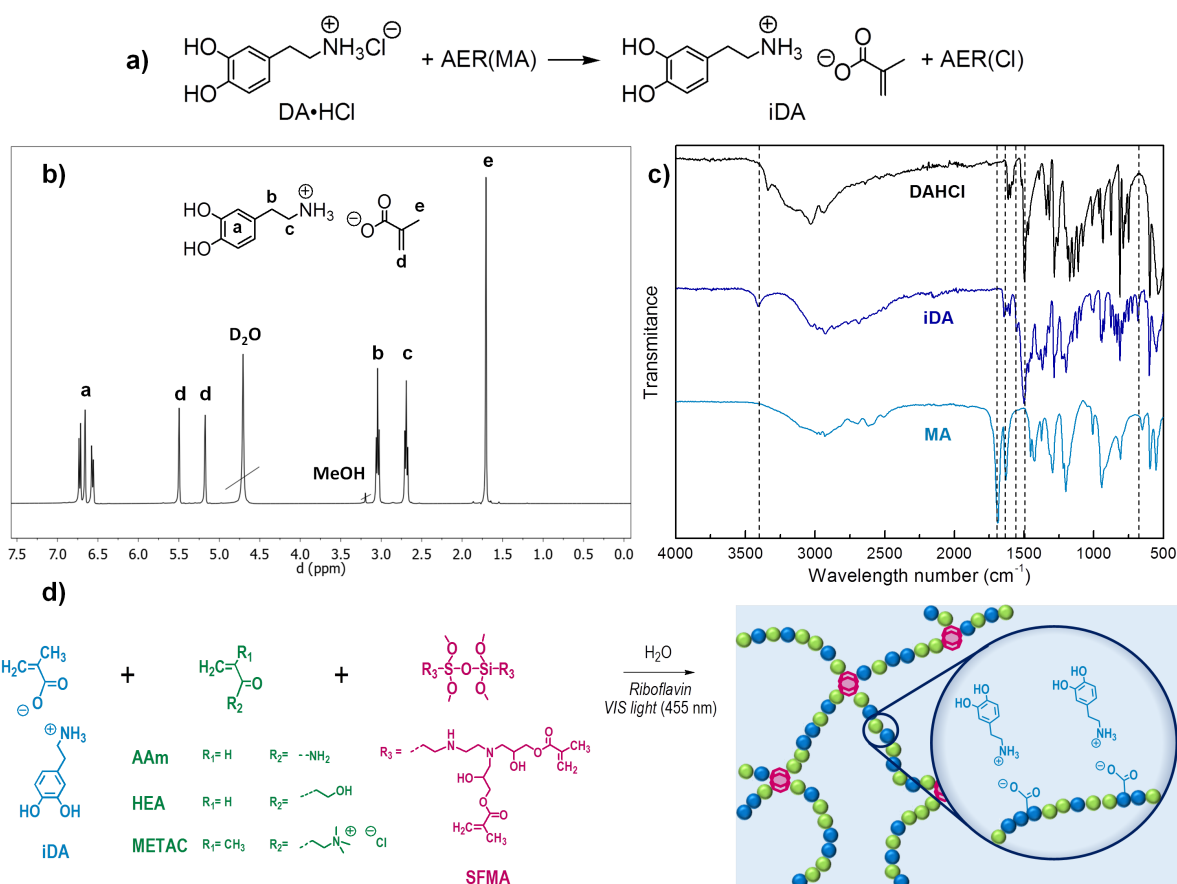
#### 3.1. Synthesis and characterization of catechol containing poly(ionic liquid) hydrogels

The catechol-containing ionic monomer, dopamine methacrylic salt (iDA) was synthesized using an ion exchange resin (AER) method from commercially available dopamine hydrochloride (DAHCl). A methanol solution of DAHCl was passed through a

chromatographic column loaded with the AER resulting in the exchange of the chloride ion for the deprotonated form of methacrylic acid as shown in Figure 1a. This simple AER method produced a highly pure ionic monomer in a nearly quantitative yield (>90% determined gravimetrically, with chloride content lower than 20 ppm, determined by the Silver chromate test).<sup>34</sup> The product was recovered in the form of a white solid readily soluble in water. iDA structure was confirmed by FTIR and <sup>1</sup>H-NMR. Resonance peaks of different hydrogens in the synthesized monomer are assigned in Figure 1b. Figure 1c shows the characteristic peaks of the new ionic monomer, iDA, and their starting reagents, DAHCl and MA: the presence of the signal at 1632 and 651 cm<sup>-1</sup> corresponds to the vinyl group from the acid (s;  $\nu_s(\text{C}=\text{C}$  vinyl); (m;  $\nu_s(=\text{C}-\text{H}$  vinyl)), these signals remain in iDA since the methacrylate group is not affected during the synthesis. The signal at 1690 cm<sup>-1</sup>, in MA spectrum, corresponds to the stretching vibration of the carboxylic group (s;  $\nu_s(\text{C}=\text{O})$ ) that disappears in the spectrum of iDA due to the higher conjugation given by the carboxylate group (m;  $\nu_s(\text{C}=\text{O})_2$ ) that appears now at 1553 cm<sup>-1</sup>. There are also some characteristic bands of DAHCl present in iDA spectrum: the signal at 1500 cm<sup>-1</sup> due to the ring stretching (m;  $\nu_s(\text{C}=\text{C}$  arom.)) and the signals at 1583 cm<sup>-1</sup> and 3405 cm<sup>-1</sup> that belong to primary amines bending and stretching modes.

Next, iDA was employed to prepare hydrogels via visible light induced copolymerization with a series of water soluble (meth)acrylate based monomers, such as HEA, AAm or METAC. SFMA, a synthesized functionalized silsesquioxane containing amines and acrylates groups was employed as co-initiator and cross-linker.<sup>35, 36</sup> Riboflavine (Rf) was incorporated as a green visible light sensitizer for the photopolymerization process. The reactions were carried out in water for 3 h with monomers concentration of 50 % w/v (see scheme in Figure 1d). The chosen photoinitiator system avoids problems associated with the presence of toxic aliphatic amines, in the final material, commonly employed as co-initiators.<sup>37</sup> The reaction yield was high in all cases producing an insoluble fraction (%IF) between 70 and 82 wt%, typical for this type of polymerizations. %IF represents the

percentage of polymer that is actually crosslinked in the hydrogel and was achieved gravimetrically through Soxhlet extraction with ultrapure THF during 24 h. Due to the good solubility of iDA in water, this photopolymerization procedure allowed to incorporate up to 50% wt of the ionic monomer in the hydrogel. The homopolymer of iDA couldn't be synthesized probably because the inhibition in polymerization reaction attributed to the presence of catechol groups. It is worth to mention also that one of the risks of this synthetic pathway is that catecholamines can follow autopolymerization in aerated basic conditions, first demonstrated by Messersmith et al. for dopamine.<sup>38</sup> Following a multistep reaction pathway, dopamine can self-polymerize via radical polymerization and produce dark polymers which are usually complex networks with free catechol groups available for further chemical reactions.<sup>39, 40</sup> In our case, the lack of brown color in the final hydrogel materials could be assumed as a primary evidence of the absence of polydopamine.<sup>8,41</sup>



**Figure 1.** (a) Scheme of ionic dopamine methacrylate (iDA) synthesis employing dopamine hydrochloride and an anion exchange resin (AER); (b)  $^1\text{H-NMR}$  spectrum of iDA in  $\text{D}_2\text{O}$  and (c) FTIR of iDA, MA and DAHCl; (d) In-situ preparation of hydrogels using VIS light polymerization, a functionalized silsesquioxane cross-linker (SFMA), ionic dopamine methacrylate (iDA), and different (meth)acrylate monomers, acrylamide (AAm), 2-hydroxyethyl acrylate (HEA) or [2-(methacryloyloxy)ethyl] trimethylammonium chloride (METAC) in the presence of Riboflavin in aqueous solution.

Table 1 summarizes the composition and properties of hydrogels prepared with variable ratios of iDA: HEA, AAm or METAC co-monomers. Hydrogels were characterized by FTIR to confirm their chemical structure. Figure S1 shows the spectra of all co-polymers and homopolymers for HEA, AAm and METAC. Characteristics bands of the ionic monomer are observed in the catechol containing poly(ionic liquid) hydrogels.<sup>25</sup> Particularly, the characteristic transmittance between  $3720$  and  $2375\text{ cm}^{-1}$  of dopamine was observed in all co-polymers containing iDA. Additionally, the co-polymers show the representative bands of each co-monomer according to the material: characteristics bands of PHEA at  $1717\text{ cm}^{-1}$  (s;  $\nu_s(\text{C=O})$ ),  $1161\text{ cm}^{-1}$  (s;  $\nu_s(\text{C-O})$ ); PAAm at  $1660\text{ cm}^{-1}$  (s;  $\nu_s(\text{C=O})$ ),  $1420\text{ cm}^{-1}$  (s;  $\nu_s(\text{C-N})$ ); PMETAC at  $1720\text{ cm}^{-1}$  (s;  $\nu_s(\text{C=O})$ ),  $500\text{-}550\text{ cm}^{-1}$  (s;  $\nu_s(\text{N-X}_i)$ ),  $1450\text{-}1480\text{ cm}^{-1}$  (s;  $\nu_s(\text{C-N})$ ) were observed in the corresponding formulations.

The polymerization process was also followed by  $^1\text{H-NMR}$ . Figure S2 shows that the polymer presents the regular spectrum of a crosslinked polymer, where the initial peaks are thicken. As an example, a de-oxygenated pre-polymeric mixture of P(HEA-co-iDA15) was irradiated for 2 h for the purpose of observing a change in the final spectra. The achieved spectra show a deformation of the initial peaks, thereby, this technique is not appropriate to characterize the polymerization process or the final material synthesized. Techniques like FTIR, SEM, swelling and DSC were employed to characterize the poly(ionic liquid) hydrogels.

**Table 1.** Composition and main characterization of poly(ionic liquid) hydrogels. Homopolymers were also synthesized as control materials.

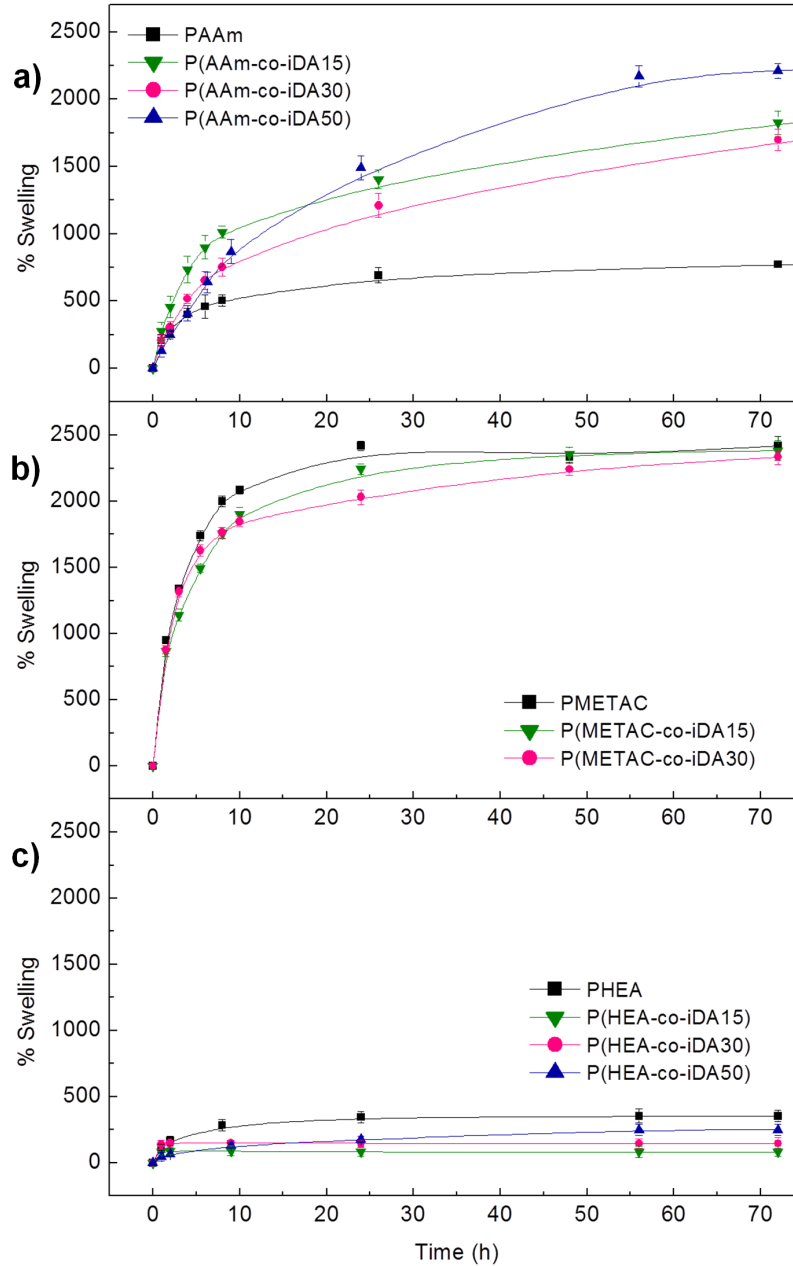
Sample	iDA (mol %)	IF(%)	Sw <sub>max</sub> (%)	n <sub>p</sub>	R	T <sub>g</sub> (°C)
HEA	0	94	353.0	0.49	0.99	2
P(HEA-co-iDA <b>15</b> )	15	70	80.8	0.08	0.92	-4
P(HEA-co-iDA <b>30</b> )	30	74	145.0	0.04	0.92	-14
P(HEA-co- iDA <b>50</b> )	50	75	230.0	0.39	0.99	6
PAAm	0	96	797.0	0.45	0.99	81
P(AAm-co- iDA <b>15</b> )	15	73	1974.0	0.67	0.99	3
P(AAm-co-iDA <b>30</b> )	30	70	1838.0	0.65	0.99	6
P(AAm-co-iDA <b>50</b> )	50	74	2298.0	0.85	0.99	11
PMETAC	0	98	2229.0	0.45	0.99	53
P(METAC-co-iDA <b>15</b> )	15	82	2357.0	0.42	0.99	-7
P(METAC-co-iDA <b>30</b> )	30	71	2242.0	0.48	0.96	-11
P(METAC-co-iDA <b>50</b> )	50	73	n.m.	n.m.	n.m.	-6

*n.m.: not measured.*

Swelling properties and internal morphology of hydrogels containing different amounts of iDA were investigated in simulated aquifer media at 25 °C.<sup>30-31,42</sup> It is worth to mention that P(METAC-co-iDA50) was not measured because of its poor mechanical stability. Figure 2 shows a quick increase in swelling during the first 10 h for all the hydrogels. Then it reached a plateau around 12 h for HEA, 24 h for METAC and 72 h for AAm. The swelling capacity of PMETAC shows no significant variation with iDA co-polymerization, this may be due the replacement of an ionic monomer (METAC) for iDA, avoiding a mayor difference with the final ionic content in the hydrogel. P(AAm-co-iDA) hydrogels present higher swelling capacity than AAm homopolymer due to a higher content of ionic



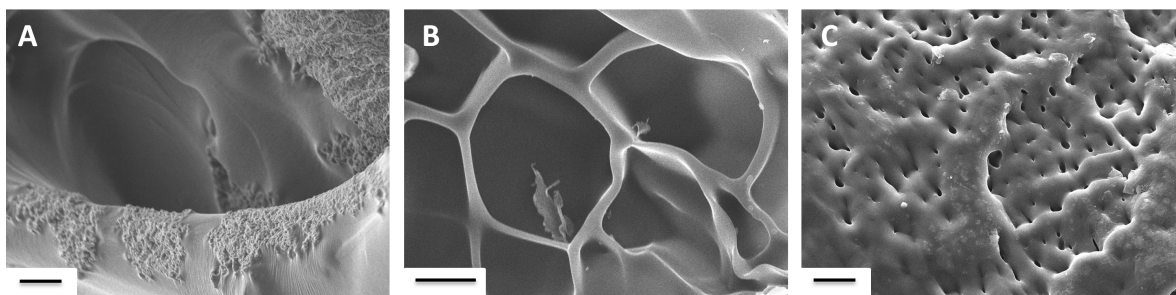
monomer within the hydrogels, a normal behavior of ionic materials during swelling. The same effect is showed in P(HEA-co-iDA) hydrogels, which present higher swelling ratio with the increase of iDA content; however, the homopolymer PHEA presents the highest swelling ratio probably due to the high osmotic pressure of the simulated solution.<sup>43,44</sup> When P(HEA-co-iDA) hydrogels are swelled in pure water, the swelling capacity increased with iDA content, as expected for the incorporation of ionic monomers. The maximum swelling capacity (between 2000 and 2500 %) was observed for P(METAC-co-iDA) and P(AAm-co-iDA) hydrogels, whereas P(HEA-co-iDA) showed swelling ratios less than 300% (see Table 1). Swelling results were fitted according to Equation 1. The diffusional exponent values,  $n_p$ , and the corresponding correlation coefficient R are summarized in Table 1. From the fitting, it can be highlighted that the correlation constant, close to 1, is indicative of the good quality of the fitting. When the value of the exponent  $n_p \leq 0.5$ , swelling follows Fick's law or is diffusional-controlled. Within experimental error, all formulations follows a Fickian behavior while P(AAm-co-iDA) shows a non-Fickian mechanism. The departure from Fick's law can be explained considering that the chains relaxation rate is higher than the solvent diffusion rate in the hydrogel, which indicates the presence of specific interactions (values of  $n_p > 0.5$ ).



**Figure 2.** Swelling curves in simulated aquifer at 25°C for **(a)** PAAm and P(AAm-co-iDA) hydrogels; **(b)** PMETAC and P(METAC-co-iDA) hydrogels and **(c)** PHEA and P(HEA-co-iDA) hydrogels.

Figure 3 shows SEM images of the internal structure of P(HEA-co-iDA15), P(AAm-co-iDA15) and P(METAC-co-iDA15) lyophilized hydrogels, previously swollen in simulated

aquifer media for 15 h. The micrographs show that the average pore size changed depending on the co-monomer when the amount of iDA was maintained constant. The average size of the pores was around  $60 \pm 15 \mu\text{m}$  for P(METAC-co-iDA15),  $25 \pm 7 \mu\text{m}$  for P(AAm-co-iDA15) and  $4 \pm 2 \mu\text{m}$  for P(HEA-co-iDA15) hydrogels. The incorporation of iDA into hydrogels also changed their internal structure. As an example, Figure S3 shows micrographs of PAAm hydrogels, where the homopolymer displays smaller pores than the co-polymer containing the ionic monomer. Next, Differential Scanning Calorimetry (DSC) was employed to characterize dry hydrogels. Figure S4a shows DSC curves for HEA hydrogels, where one single glass transition temperature at  $2 \text{ }^\circ\text{C}$  was observed for the homopolymer. When iDA was incorporated, the values of  $T_g$  decreased to  $-4 \text{ }^\circ\text{C}$  for P(HEA-co-iDA15) and  $-14 \text{ }^\circ\text{C}$  for P(HEA-co-iDA30), but a broadening and an increase of  $T_g$  to  $6 \text{ }^\circ\text{C}$  is observed finally for P(HEA-co-iDA50). This behavior was attributed to the mobility of the chains that result from the competition between the steric effect associated with the presence of a bulky group (more mobility) and the strong polar interactions established by the ionic monomer group (less mobility).<sup>45</sup> At low concentrations of the ionic monomer, the steric effect is dominant resulting in a decrease of  $T_g$ , whereas at high iDA concentrations the polar interactions play a key role increasing  $T_g$  values. Similar trends were observed for hydrogels containing AAm and METAC (see Table 1 and Figure S4b-c).



**Figure 3.** Scanning electron microscopy of lyophilized poly(ionic liquid) hydrogels, (A) P(METAC-co-iDA15), (B) P(AAm-co-iDA15) and (C) P(HEA-co-iDA15). Scale bar:  $10 \mu\text{m}$ .

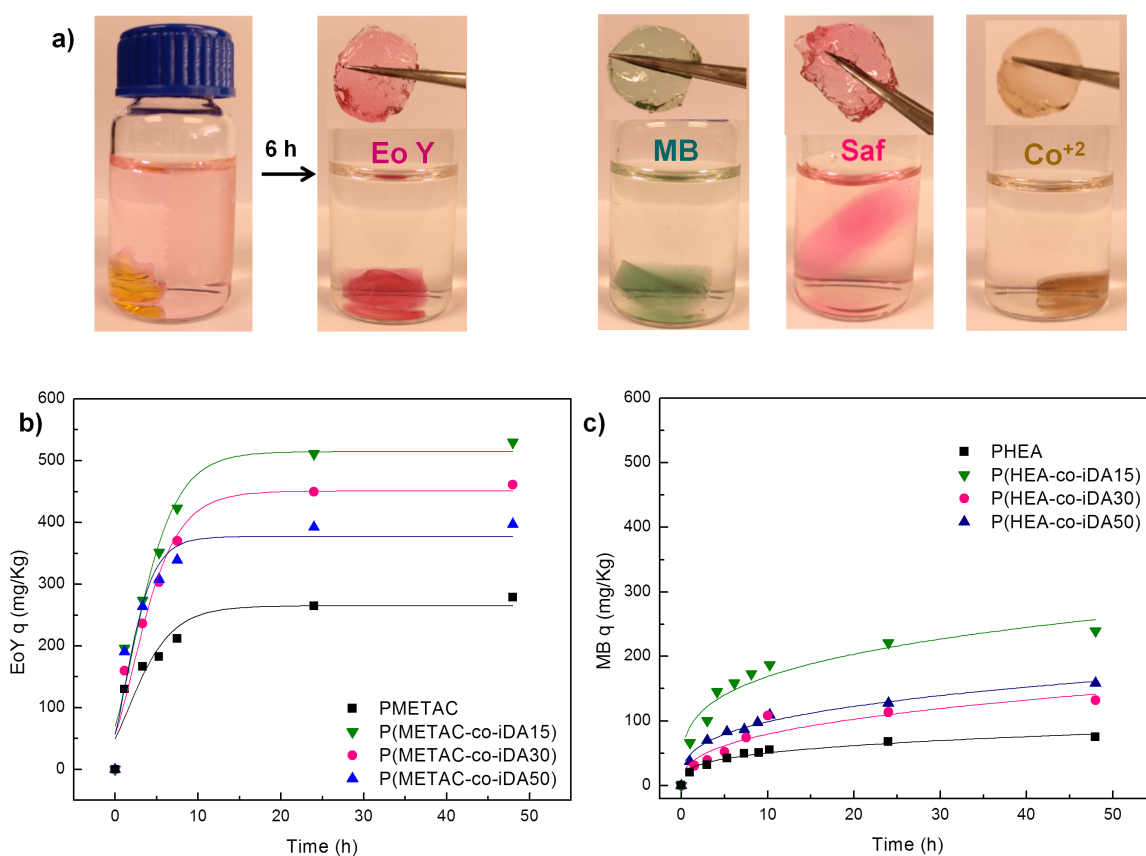
One potential drawback of the catechol/dopamine ionic functional hydrogels is the possible leaching of the dopamine cationic moiety which is ionically interacting with the anionically charged polymer backbone. To evaluate this, samples of iDA containing hydrogels (as prepared without washing) were placed in different vials and immersed in aqueous solutions at pH ranging from 2 to 12. Simultaneously, iDA monomer (same amount as presented in the gel samples) was dissolved in aqueous solutions at the same pH values (see Figure S5). The presence of free dopamine in basic solution is associated by the appearance of a brownish color due to the spontaneous formation of polydopamine structures with extended  $\pi$  conjugation; this formation is accelerated at pH values above 6.<sup>8</sup>

<sup>38</sup> As expected, after 8 h at ambient temperature, reference vials containing free iDA monomer showed a clear brownish color associated to the polydopamine that was more intense with increasing pH. Interestingly, the vials containing iDA acrylic hydrogels were colorless at all pH values. These results confirm that the catechol/dopamine moiety of iDA containing hydrogels does not leach when gels are swollen in water and show evidence that the leaching or formation of polydopamine structures is precluded within the swollen gels. FTIR was also employed to confirm the lack of leaching of catechol groups. A dried P(HEA-co-iDA50) hydrogel (as prepared before washing) was immersed in the simulated aquifer solution during 24 h to compare the spectra before and after the contact of the material with the aqueous solution. After the contact with the solvent the hydrogel was dried at 48°C during 24 h. As confirmed by Figure S6, the spectrum taken after the assay kept the chemical structure and the same characteristics bands for the polymer composed of HEA and iDA. This result demonstrates the stability of the catechol moiety into the hydrogels.

### **3.2. Application of catechol containing poly(ionic liquid) hydrogels in water purification**

As a potential application, the pollutant removal capacity of catechol-containing poly(ionic liquid) hydrogels was tested to evaluate their potential use in water purification

systems. The synthesized hydrogels were immersed into a series of simulated aquifer solutions, each of them containing the following pollutants: the organic anionic dye Eosin Y (EoY), organic cationic dyes like Methylene blue (MB) and Safranin (Saf), and heavy metals like  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$  and the oxoanions of As(V) and Cr(VI). Preliminary tests in simulated aquifer solutions containing concentrations of contaminants 100 times higher than the allowed values showed that the solutions became completely colorless after 6 hours, while the color is retained into the hydrogels (Figure 4a).

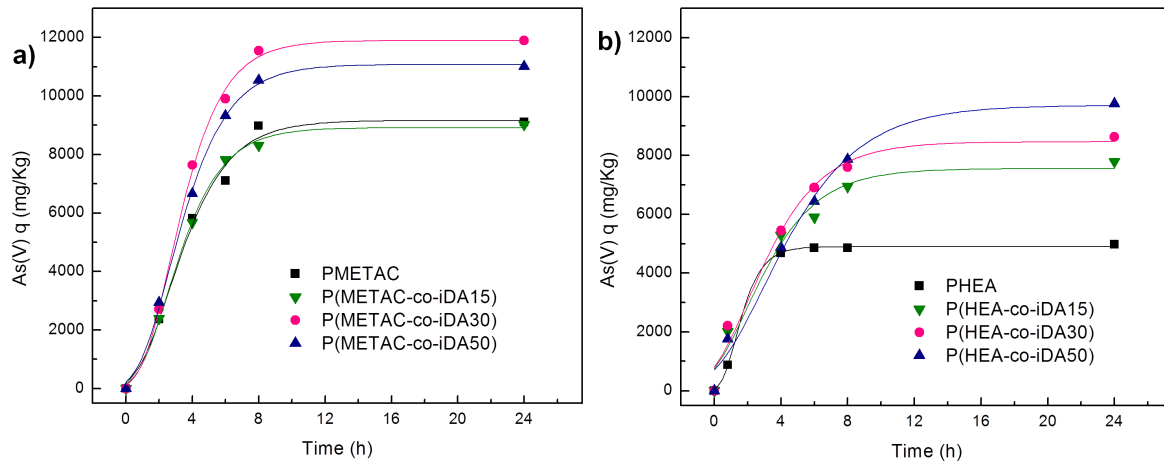


**Figure 4.** (a) Upper: photographs of different contaminants solution before and after 6 h of contact with P(HEA-co-iDA30), Eosin Y (EoY), Methylene Blue (MB), Safranin (Saf) and Cobalt salt ( $\text{Co}^{2+}$ ); (b) Removal kinetics of EoY from P(METAC-co-iDA) hydrogels; (c) Removal kinetics of methylene blue (MB) from P(HEA-co-iDA) hydrogels.

Quantitative determinations were performed using UV-Vis absorption spectroscopy to determine the concentration of selected pollutants as a function of time. The analytical concentration of contaminants in the screening experiments were [EoY] = 0.0025 mg mL<sup>-1</sup>, [MB] = 0.01 mg mL<sup>-1</sup>, [Cr(VI)] = 0.002 mg mL<sup>-1</sup> and [As(V)] = 0.13 mg mL<sup>-1</sup>. In all cases, 10 mL of solution were incubated with a ~10 mg hydrogel disc for 24 h at room temperature. After incubation, hydrogels were removed and the concentration of the remaining pollutant in solution was evaluated spectroscopically. Control experiments without hydrogels were also performed to assess the stability of contaminants solutions. Table 2 and Table S1 collect the experimental results expressed as  $q$  (capacity of pollutants removal established per unit mass of hydrogels - Equation 2). To qualitatively describe the adsorption process, the experimental data were fitted by pseudo-first-order kinetic model, known as Lagergren kinetic rate equation on adsorption processes (Equation 4).<sup>33</sup> The following conclusions can be drawn from analysis of the results shown in Table S1. As expected, hydrogels containing METAC and AAm do not adsorb MB and EoY respectively. This is presumably due to the predominant role that electrostatic repulsive forces play in these systems and the fact that MB/METAC and EoY/AAm pairs are positively and negatively charged under the experimental conditions. METAC groups are positively charged in P(METAC-co-iDA) hydrogels at pH 6, whereas AAm could be partially hydrolyzed as carboxylate groups,<sup>35</sup> because of the presence of catecholamines. This could be the explanation for the negative results, even though it is important to take into account that interactions between organic dyes and sorbents are complexes and not always directly related with electrostatic interactions.<sup>46, 47</sup> For positive results, it is worth to remark that most iDA containing hydrogels show a higher dye removal capacity than their respective homopolymers. The dye removal capacity (at equilibrium) of iDA containing hydrogels is not directly proportional to the amount of iDA. This can be rationalized considering the different swelling properties of hydrogels and a number of interactions such

as Van der Waals, hydrogen-bonding, and electrostatic forces play a role in the contaminant adsorption process. MB  $q$  values for our gels are similar to those reported for P(AAm-co-MMA) whereas EoY  $q$  values are higher than those reported by Milli et.al.<sup>48, 49</sup> Adsorption time is an important parameter in any removal processes. Thus, kinetic studies in simulated aquifer solution at 25°C were performed for EoY and MB (Figure 4b-c and Table S1). High initial adsorption rates were observed for MB and EoY and both dyes were completely removed after 5 h for most gels under the experimental conditions. Pseudo first order kinetic constants ( $k$ ) for dye adsorption by HEA based hydrogels are not affected by the presence of iDA, whereas  $k$  values for AAm and METAC hydrogels containing iDA are higher than that of the corresponding homopolymers. Reusability assays are planned to be developed in future works, however some preliminary experiments were carried out for EoY and MB. Both dyes are desorbed in a 60% in 4 h, nearly, from P(HEA-co-iDA15) hydrogels in methanol, which may indicate the possibility of reusability of these materials. Qualitative results in Figure S7.

Interestingly, the iDA containing hydrogels showed excellent results in the cases of pollutant metal ions such as As(V) and Cr(VI) (Figure 5a-b). Removal kinetics for the adsorption of As(V) and Cr(VI) are summarized in Table 2. As it can be seen,  $q$  values increase with increasing the amount of iDA co-polymers for both heavy metal ions. Kinetic profiles (in METAC and HEA based hydrogels) for As(V) removal and gel swelling are similar, suggesting that the speed of heavy metal adsorption is in part limited by the gel swelling process. It is worth to remark that these  $q$  values are compared favorably with the highest performing hydrogels in the literature based on lays and chitin based hydrogels. Catechol containing poly(ionic liquid) hydrogels benefit from the outstanding metal chelating ability of catechols groups showing a great potential for heavy metal removal<sup>50, 51</sup> and preserving their ability to remove organic compounds with different charge.



**Figure 5.** (a) Removal kinetics of As(V) from P(METAC-co-iDA) hydrogels; (b) Removal kinetics of As(V) from P(HEA-co-iDA) hydrogels.

**Table 2.**  $q$  capacity of As(V) and Cr(VI) from the hydrogels. Kinetic study of As(V).

Hydrogel	$q$ As(V) ( $\lambda^{\max}$ 880 nm) (mg Kg <sup>-1</sup> )	$k$ (h <sup>-1</sup> )	$R$	$q$ Cr(VI) ( $\lambda^{\max}$ 540 nm) (mg Kg <sup>-1</sup> )
PHEA	4976	0.68	0.92	122
P(HEA-co-iDA15)	7793	0.28	0.97	851
P(HEA-co-iDA30)	8638	0.28	0.99	1543
P(HEA-co-iDA50)	9766	0.24	0.99	2001
PAAm	n.r.	n.m.	-	30
P(AAm-co-iDA15)	1428	n.m.	-	378
P(AAm-co-iDA30)	1198	n.m.	-	721
P(AAm-co-iDA50)	2475	n.m.	-	955
PMETAC	9099	0.30	0.98	25
P(METAC-co-iDA15)	9008	0.39	0.98	752
P(METAC-co-iDA30)	11889	0.38	0.99	1332
P(METAC-co-iDA50)	11009	0.39	0.97	1843

*n.r.: no removal; n.m.: not measured*

#### 4. CONSLUSIONS



In this work new catechol containing poly(ionic liquid) hydrogels showed to be effective for the removal of different contaminants of diverse charge and nature. For this purpose, a new water soluble ionic dopamine methacrylate monomer (iDA) was successfully incorporated into acrylic hydrogels via visible light photopolymerization in a low energetic pathway. The incorporation of iDA allowed to prepare poly(ionic liquid) hydrogels with the highest content of catechol groups in hydrogels reported up to date, as high as 50% mol and confer synergic adsorption properties to the hydrogels compared with acrylic homopolymer. Characterization of the final materials show the stability of the formulations with absence of significant leaching of the dopamine cationic moiety from the poly(ionic liquid) hydrogel.

Catechol-containing poly(ionic liquid) hydrogels were tested for the removal of different organic contaminants owing different charges and heavy metal ions from simulated aquifer solution. In particular, the synthesized hydrogels were highly effective for the removal of As(V) and Cr(VI) showing higher efficiency than other materials reported in the literature up to date. All in all, this paper demonstrates the potential combination of catechol and poly(ionic liquid) chemistries for water purification purposes.

## ASSOCIATED CONTENT

### **Supporting information**

Additional experimental results are included in the support information, including more SEM images, FTIR and DSC results of the hydrogels. <sup>1</sup>H-NMR spectrum of the pre-polymeric solution and the polymerized hydrogel of P(HEA-co-iDA15) are included. Also, FTIR analysis and pictures for the leaching assays are presented. Finally, some pictures for a potential reusability development are showed. This material is available on the Web at <http://pubs.acs.org>.

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## Author Contributions

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## Notes

The authors have no competing financial interests.

## REFERENCES

- (1) Ai, Y.; Nie, J.; Wu, G.; Yang, D. The DOPA-Functionalized Bioadhesive with Properties of Photocrosslinked and Thermoresponsive. *Journal of Applied Polymer Science* **2014**, *131*, 41102.
- (2) Skelton, S.; Bostwick, M.; O'Connor, K.; Konst, S.; Casey, S.; Lee, B. P. Biomimetic adhesive containing nanocomposite hydrogel with enhanced materials properties. *Soft Matter* **2013**, *9*, 3825-3833.
- (3) Faure, E.; Falentin-Daudré, C.; Jérôme, C.; Lyskawa, J.; Fournier, D.; Woisel, P.; Detrembleur, C. Catechols as versatile platforms in polymer chemistry. *Progress in Polymer Science* **2013**, *38*, 236-270.

- (4) Waite Jh Fau - Tanzer, M. L.; Tanzer, M. L. Polyphenolic Substance of *Mytilus edulis*: Novel Adhesive Containing L-Dopa and Hydroxyproline. *Science* **1981**, *212*, 36-8075.
- (5) Chung, H.; Grubbs, R. H. Rapidly Cross-Linkable DOPA Containing Terpolymer Adhesives and PEG-Based Cross-Linkers for Biomedical Applications. *Macromolecules* **2012**, *45*, 9666-9673.
- (6) Zeng, Z.; Wang, H.; Morsi, Y.; Mo, X. Synthesis and characterization of incorporating mussel mimetic moieties into photoactive hydrogel adhesive. *Colloids and Surfaces B: Biointerfaces* **2018**, *161*, 94-102.
- (7) Patil, N.; Aqil, A.; Ouhib, F.; Admassie, S.; Inganas, O.; Detrembleur, C.; Jérôme, C. Bioinspired redox-active catechol-bearing polymers as ultrarobust organic cathodes for lithium storage”, *Adv. Mater.* **2017**, *29*, 1703373.
- (8) Patil, N.; Jérôme, C.; Detrembleur, C. Recent advances in the synthesis of catechol-derived (bio)polymers for applications in energy storage and environment. *Progress in Polymer Science* **2018**, *82*, 34-91.
- (9) Jeong, Y. K.; Park, S. H.; Choi, J. W. Mussel-Inspired Coating and Adhesion for Rechargeable Batteries: A Review. *ACS Applied Materials & Interfaces* **2018**, *10*, 7562-7573.
- (10) Han, L.; Gong, L.; Chen, J.; Zhang, J.; Xiang, L.; Zhang, L.; Wang, Q.; Yan, B.; Zeng, H. A.-O. h. o. o. Universal Mussel-Inspired Ultrastable Surface-Anchoring Strategy via Adaptive Synergy of Catechol and Cations. *ACS Applied Materials & Interfaces* **2018**, *10*, 1944-8252.
- (11) Cheng, H.; Yue, K.; Kazemzadeh-Narbat, M.; Liu, Y.; Khalilpour, A.; Li, B.; Zhang, Y. S. A.-O. h. o. o. X.; Annabi, N.; Khademhosseini, A. A.-O. h. o. o. Mussel-Inspired Multifunctional Hydrogel Coating for Prevention of Infections and Enhanced Osteogenesis. *ACS Applied Materials & Interfaces* **2017**, *9*, 1944-8252.
- (12) Hongguang, S.; Yanqiu, Z.; Hussain, S.; Jun, M; Yongping, B.; Xi, S.; Jang-Kyo K.; Lu, S. Novel mussel-inspired zwitterionic hydrophilic polymer to boost membrane water-treatment performance. *Journal of Membrane Science* **2019**, *582*, 376-388.

- (13) Jiang, X.; Li, S.; Bai, Y.; Shao, L. Ultra-facile aqueous synthesis of nanoporous zeolitic imidazolate framework membranes for hydrogen purification and olefin/paraffin separation. *Journal of Materials Chemistry A* **2019**, *7*, 10898-10904.
- (14) Ajjan, F. N.; Ambrogi, M.; Tiruye, G. A.; Cordella, D.; Fernandes, A. M.; Grygiel, K.; Isik, M.; Patil, N.; Porcarelli, L.; Rocasalbas, G.; Vendramiento, G.; Zeglio, E.; Antonietti, M.; Detrembleur, C.; Inganäs, O.; Jérôme, C.; Marcilla, R.; Mecerreyes, D.; Moreno, M.; Taton, D.; Solin, N.; Yuan, J. Innovative polyelectrolytes/poly(ionic liquid)s for energy and the environment. *Polymer International* **2017**, *66*, 1119-1128.
- (15) Yu, H.; Zhang, C.; Anderson, J. L. Ionic Liquids and Polymeric Ionic Liquids in Analytical Environmental Applications. In *Applications of Ionic Liquids in Polymer Science and Technology*; Mecerreyes, D., Ed.; Springer Berlin Heidelberg: Berlin, Heidelberg, 2015; pp 153-198.
- (16) Isik, M.; Fernandes, A. M.; Vijayakrishna, K.; Paulis, M.; Mecerreyes, D. Preparation of poly(ionic liquid) nanoparticles and their novel application as flocculants for water purification. *Polymer Chemistry* **2016**, *7*, 1668-167.
- (17) Zhang, W.; Zhao, Q.; Yuan, J. Porous Polyelectrolytes: The Interplay of Charge and Pores for New Functionalities. *Angewandte Chemie International Edition* **2018**, *57*, 6754-6773.
- (18) Guo, J.; Qiu, L.; Deng, Z.; Yan, F. Plastic reusable pH indicator strips: preparation via anion-exchange of poly(ionic liquids) with anionic dyes. *Polymer Chemistry* **2013**, *4*, 1309-1312.
- (19) Ali, I. New Generation Adsorbents for Water Treatment. *Chemical Reviews* **2012**, *112*, 105073-509.
- (20) Li, B.; Lai, C.; Zeng, G.; Qin, L.; Yi, H.; Huang, D.; Zhou, C.; Liu, X.; Pheng, M.; Xu, P.; Zhang, C.; Huang, F.; Liu, S. Facile Hydrothermal Synthesis of Z-Scheme Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub>/Bi<sub>2</sub>WO<sub>6</sub> Heterojunction Photocatalyst with Enhanced Visible Light Photocatalytic Activity. *ACS Applied Materials & Interfaces* **2018**, *10*, 18824-18836.
- (21) Palermo, E. Underwater maids: Mussels and clams could mop up waterways. **2014**, [www.lifescience.com](http://www.lifescience.com)

- (22) Ismail, N. S.; Müller, C. E.; Morgan, R. R.; Luthy, R. G. Uptake of Contaminants of Emerging Concern by the Bivalves *Anodonta californiensis* and *Corbicula fluminea*. *Environmental Science & Technology* **2014**, *48*, 9211-9219.
- (23) Patil, N.; Aqil, M.; Aqil, A.; Ouhib, F.; Marcilla, R.; Minoia, A.; Lazzaroni, R.; Jérôme, C.; Detrembleur, C. Integration of Redox-Active Catechol Pendants into Poly(ionic liquid) for the Design of High-Performance Lithium-Ion Battery Cathodes. *Chemistry of Materials* **2018**, *30*, 5831-5835.
- (24) Lee, B. P.; Huang K Fau - Nunalee, F. N.; Nunalee Fn Fau - Shull, K. R.; Shull Kr Fau - Messersmith, P. B.; Messersmith, P. B. Synthesis of 3,4-dihydroxyphenylalanine (DOPA) containing monomers and their co-polymerization with PEG-diacrylate to form hydrogels. *Journal of Biomaterials Science, Polymer Edition* **2004**, *15*, 920-5063.
- (25) Park, J. K.; Kim, K. S.; Yeom, J.; Jung, H. S.; Hahn, S. K. Macromol. Chem. Phys. 20/2012. *Macromolecular Chemistry and Physics* **2012**, *213*, 2093-2093.
- (26) Marcisz, K.; Romanski, J.; Stojek, Z.; Karbarz, M. Environmentally sensitive hydrogel functionalized with electroactive and complexing-iron(III) catechol groups. *Journal of Polymer Science Part A: Polymer Chemistry* **2017**, *55*, 3236-3242.
- (27) Gómez, M. L.; Gallastegui, A.; Spesia, M. B.; Montejano, H. A.; Williams, R. J.; Previtali, C. M. Synthesis of poly(HEMA-co-AAm) hydrogels by visible-light photopolymerization of aqueous solutions containing aspirin or ibuprofen: analysis of the initiation mechanism and the drug release. *Polymers for Advanced Technologies* **2017**, *28*, 435-442.
- (28) Lenoble, V.; Deluchat V Fau - Serpaud, B.; Serpaud B Fau - Bollinger, J.-C.; Bollinger, J. C. Arsenite oxidation and arsenate determination by the molybdene blue method. *Talanta* **2003**, *61*, 267-273.
- (29) Dean, J. A.; Beverly, M. L. Extraction and Colorimetric Determination of Chromium with 1,5-Diphenylcarbohydrazide. *Analytical Chemistry* **1958**, *30*, 977-979.
- (30) Davidsoniii, G.; Peppas, N. A. Solute and penetrant diffusion in swellable polymers. V. Relaxation-controlled transport in P(HEMA-co-MMA) copolymers. *Journal of Control Release* **1986**, *3*, 243-258.

- (31) Ritger, P. L.; Peppas, N. A. A simple equation for description of solute release II. Fickian and anomalous release from swellable devices. *Journal of Controlled Release* **1987**, *5*, 37-42.
- (32) Organization, W. H. *Guidelines for Drinking-Water Quality*, 2008; Vol. 1.
- (33) Lagergren, S. Zur theorie der sogenannten adsorption gelöster stoffe [about the theory of so-called adsorption of soluble substances]. *Kungliga Svenska Vetenskapsakademiens*, **2019**, *4*, 1-39.
- (34) Toral, A. R.; de los Ríos, A. P.; Hernández, F. J.; Janssen, M. H. A.; Schoevaart, R.; van Rantwijk, F.; Sheldon, R. A. Cross-linked *Candida antarctica* lipase B is active in denaturing ionic liquids. *Enzyme and Microbial Technology* **2007**, *40*, 1095-1099.
- (35) Gómez, M. L.; Fasce, D. P.; Williams, R. J. J.; Erra-Balsells, R.; Kaniz Fatema, M.; Nonami, H. Silsesquioxane functionalized with methacrylate and amine groups as a crosslinker/co-initiator for the synthesis of hydrogels by visible-light photopolymerization. *Polymer* **2008**, *49*, 3648-3653.
- (36) Gallastegui, A.; Spesia, M. B.; dell'Erba, I. E.; Chesta, C. A.; Previtali, C. M.; Palacios, R. E.; Gómez, M. L. Controlled release of antibiotics from photopolymerized hydrogels: Kinetics and microbiological studies. *Materials Science and Engineering: C* **2019**, *102*, 896-905.
- (37) Greim, H.; Bury D Fau - Klimisch, H. J.; Klimisch Hj Fau - Oeben-Negele, M.; Oeben-Negele M Fau - Ziegler-Skylakakis, K.; Ziegler-Skylakakis, K. Toxicity of aliphatic amines: structure-activity relationship. *Chemosphere* **1998**, *2*, 271-295.
- (38) Lee, H.; Dellatore, S. M.; Miller, W. M.; Messersmith, P. B. Mussel-inspired surface chemistry for multifunctional coatings. *Science (New York, N.Y.)* **2007**, *318*, 426-430.
- (39) Herlinger, E.; Jameson, R. F.; Linert, W. Spontaneous autoxidation of dopamine. *Journal of the Chemical Society, Perkin Transactions 2* **1995**, *0*, 259-263.
- (40) Faure, E.; Falentin-Daudré, C.; Jérôme, C.; Lyskawa, J.; Fournier, D.; Woisel, P.; Detrembleur, C. Catechols as versatile platforms in polymer chemistry. *Progress in Polymer Science* **2013**, *38*, 236-270.
- (41) d'Ischia, M.; Napolitano A Fau - Ball, V.; Ball V Fau - Chen, C.-T.; Chen Ct Fau - Buehler, M. J.; Buehler, M. J. Polydopamine and eumelanin: from structure-property

relationships to a unified tailoring strategy. *Accounts of Chemical Research* **2014**, *12*, 1520-4898.

(42) Michailova, V.; Titeva, S.; Kotsilkova, R.; Krusteva, E.; Minkov, E. Water uptake and relaxation processes in mixed unlimited swelling hydrogels. *International Journal of Pharmaceutics* **2000**, *209*, 45-56.

(43) Horkay, F.; Tasaki, I.; Basser, P. J. Osmotic Swelling of Polyacrylate Hydrogels in Physiological Salt Solutions. *Biomacromolecules* **2000**, *1*, 84-90.

(44) Yarimkaya, S.; Basan, H. Synthesis and Swelling Behavior of Acrylate-Based Hydrogels. *Journal of Macromolecular Science, Part A* **2007**, *44*, 699-706.

(45) Mohan, Y. M.; Murthy, P. S. K.; Raju, K. M. Synthesis and swelling behaviour of interpenetrating network polymers of poly(vinyl alcohol) and poly(acrylamide-co-potassium methacrylate). *Designed Monomers and Polymers* **2005**, *8*, 187-202.

(46) Cui, L.; Jia, J.; Guo, Y.; Liu, Y.; Zhu, P. Preparation and characterization of IPN hydrogels composed of chitosan and gelatin cross-linked by genipin. *Carbohydrate polymers* **2014**, *99*, 31-38.

(47) V Dadhaniya, P.; Patel, M.; Patel, R. Swelling and dye adsorption study of novel superswelling [Acrylamide/N-vinylpyrrolidone/3(2-hydroxyethyl carbamoyl) acrylic acid] hydrogels. *Polymer Bulletin* **2006**, *57*, 21-31.

(48) Mittal, H.; Maity, A.; Ray, S. S. Effective removal of cationic dyes from aqueous solution using gum ghatti-based biodegradable hydrogel. *International Journal of Biological Macromolecules* **2015**, *79*, 8-20.

(49) Milli, L.; Zanna, N.; Merletti, A.; Di Giosia, M.; Calvaresi, M.; Focarete, M. L.; Tomasini, C. Pseudopeptide-Based Hydrogels Trapping Methylene Blue and Eosin Y. *Chemistry – A European Journal* **2016**, *22*, 12106-12112.

(50) Waiman, C. V.; dell'Erba, I. E.; Chesta, C. A.; Gómez, M. L. Hybrid mineral@silsesquioxane particles for water remediation: synthesis, characterization and application as adsorbent of As(V) and other water pollutants. *Journal of Materials Science* **2018**, *53*, 12781-12794.

(51) Luz Peralta Ramos, M.; González, J.; G. Albornoz, S.; Pérez, C. J.; Villanueva, E.; Giorgieri, S.; Copello, G. Chitin hydrogel reinforced with TiO<sub>2</sub> nanoparticles as an arsenic sorbent. *Chemical Engineering Journal* **2016**, *285*, 581-587.

## Table of Contents /Abstract graphics

