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

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KEYWORDS: *bioinspired materials, catechols, poly(ionic liquid)s, hydrogels, water
purification, heavy metal removal.*

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3 **ABSTRACT:** Mussel inspired catechol containing materials have currently drawn great
4 attention as biomaterials, adhesives, surface coatings and in bioelectronics, among other
5 applications. In this work, we mimicked the ability of mussels as water filtration systems to
6 adsorb organic and inorganic contaminants. For this purpose, the synthesis of biomimetic
7 hydrogels by co-polymerization of a new ionic monomer, dopamine methacrylic acid salt
8 (iDA) with a series of water soluble methacrylate monomers was performed using visible
9 light photopolymerization. The iDA ionic monomer is highly water soluble as compared to
10 previous reported monomers containing catechol groups. This allows its incorporation into
11 different acrylic hydrogels in concentrations up to 50 % mol of monomers containing
12 catechol groups, leading to functional materials with variable morphology and swelling
13 properties. The hydrogels displayed to be highly effective for the removal of heavy metals
14 such as As(V) and Cr(VI) with very good effectiveness compared to other commonly
15 employed natural sorbents, such as clays. Additionally, these poly(ionic liquid) hydrogels
16 containing catechol groups were evaluated in the removal also of other pollutants such as
17 charged organic dyes. Preliminarily results demonstrate the versatility of these materials
18 that combine catechol and ionic chemistry for the adsorption of a wide variety of water
19 pollutants.
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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.^{1, 2} The inspiration came from the proteins secreted by mussels which can strongly attach to a wide variety of substrates.^{3, 4} 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 and even batteries.^{3, 5-13} Furthermore, the incorporation of new cations and anions moieties into polymeric materials is giving rise to a new and novel family of functional polymers named poly(ionic liquid)s. Poly(ionic liquid)s have expanded the applications and properties of both common polyelectrolytes and molecular ionic liquids. They have become an emerging interdisciplinary topic in polymer chemistry and physics, catalysis, materials science, separation, electrochemistry and analytical chemistry.¹⁴ 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,¹⁵ water flocculants for water filtration,¹⁶ porous absorbents,¹⁷ anionic dyes absorbers and pH indicators.¹⁸

In general, pollutants removal methods are based on chemical oxidation, coagulation, flotation, chemical or biological degradation, among others.¹⁹ However, recent studies have shown that purification techniques currently used are not totally effective. Thus, new materials have been synthesized to improve removal efficiencies.²⁰ In particular, adsorption is considered one of the most suitable water treatment methods due to its simple application and the wide range of adsorbents that can be employed. Consequently, the development of new adsorbents with improved properties, such as: rapid adsorption speed, high adsorption

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3 capacity and mechanically resistant, has generated a big interest in the development of new
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5 polymeric adsorbent materials based on hydrogels.¹⁹
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8 In addition to its excellent adherence to rocks, mussels are recognized as natural water
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10 filtration systems, constantly sieving the water for a meal of bacteria or microscopic algae.
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12 As they filter water, the tissues of the bivalves absorb pathogens and chemicals such as:
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14 herbicides, pharmaceuticals, and flame retardants, among others.^{21, 22} This inspired us to
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16 combine catechol polymer chemistry within new poly(ionic liquid)s as new polymeric
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18 materials for water purification. Recently, this combination was proposed by Detrembleur
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20 et al. to be used in new materials for energy applications.²³ Herein, we decided to develop a
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22 new platform of hydrogels functionalized both by catechol and ionic moieties. Monomers
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24 containing catechol groups, such as dopamine methacrylamide or 4-vinyl catechol, are
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26 usually co-polymerized in a protected form via a free-radical polymerization with vinyl
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28 monomers.²⁴⁻²⁶ However, in the case of hydrogels, the incorporation of catechol co-
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30 monomers is restricted to less than 20% mol due to the poor water solubility of
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32 (co)polymers containing catechol.
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38 To overcome this limitation in the functionalization degree of the hydrogels with catechol
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40 groups, in this paper we designed a highly water soluble catechol-containing ionic
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42 monomer, dopamine methacrylic salt (iDA). Then, a new family of acrylic hydrogels was
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44 synthesized by photo co-polymerization of iDA with acrylic monomers in water solutions
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46 employing a vitamin as sensitizer (Riboflavine) and blue LEDs as irradiation source. We
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48 chose this synthetic method because of its green aspects and its low energy requirements
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50 and versatility. This paper presents the synthesis and characterization of the catechol
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52 poly(ionic liquid) hydrogels with three different co-monomers, acrylamide (AAm), [2-
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54 (methacryloyloxy) ethyl] trimethylammonium chloride (METAC) and 2-hydroxyethyl
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3 acrylate (HEA). Additionally, swelling studies as a function of hydrogel composition are
4 presented. Finally, the potential use of our gels in pollutant removal applications was
5 explored obtaining promising results for the adsorption of heavy metals and organic
6 compounds.
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16 **2. EXPERIMENTAL SECTION**

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18 **2.1 Materials and Methods.** An anionic exchange resin (AER) from Alfa Aesar
19 (Amberlyst A-26 (OH), 0.8 mol L⁻¹), commercial methacrylic acid (MA) from Sigma
20 Aldrich and dopamine hydrochloride (DAHCl) from Alfa Aesar were employed for the
21 synthesis of the new ionic monomer.
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27 2-Hydroxyethylacrylate (HEA) (~ 96%), acrylamide (AAm) (~ 99%) and [2-
28 (methacryloyloxy) ethyl] trimethylammonium chloride (METAC, 80% in water) (~ 97%),
29 were obtained from Sigma-Aldrich and used for the synthesis of the hydrogels.
30 Polymerization inhibitors (quinone derivatives) were removed through the passage of liquid
31 monomers through a column containing an exchange resin (De-Hibit-200® from
32 Polyscience Inc.). A functionalized silsesquioxane with amino and methacrylate groups
33 (SFMA) synthesized in our laboratory was employed as co-initiator and cross-linking
34 agent.²⁷ Riboflavin (Rf, 98%) (Vitamin B2) was obtained from Sigma-Aldrich and was
35 used as a natural sensitizer.
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47 Simulated aquifer solution was prepared with 0.1M of NaCl from Sigma Aldrich at pH 6
48 (regulated with HCl).
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52 Commercial organic dyes (Sigma Aldrich) were employed to simulate textile wastes:
53 Eosin Y (~99%) (EoY), Methylene Blue (~99%) (MB) and Safranin (~99%) (Saf).
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3 Employed inorganic salts were: CoCl_2 (~99.99%), $\text{Cu}(\text{NO}_3)_2$ (~99.99%), $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$
4 (~98%) from Sigma Aldrich, and $\text{K}_2\text{Cr}_2\text{O}_7$ (~98%) from Merck.
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7 The phosphomolibdate method was employed for the colorimetric detection of As(V).
8 Ascorbic acid, sodium tartrate and sodium molibdate, all from Merck, were employed as
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10 received for the colorimetric detection of Cr(VI); 1,5-Diphenylcarbazide from Sigma
11 Aldrich was employed as indicator and complexing compound.^{28, 29}
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17 **2.2 Synthesis of dopamine methacrylic acid salt (iDA).** The synthesis of iDA was
18 carried out using an anionic exchange resin (AER), (exchange capacity 0.8 mol L^{-1}), an
19 excess (>10% w/v) of commercial methacrylic acid, water and 0.05M of dopamine chloride
20 in methanol. The AER column was loaded with an excess of methacrylic acid solution
21 (>10% w/v). Then, a 0.05M of dopamine chloride solution in methanol was passed slowly
22 through the column. The final product, dopamine methacrylate (iDA), was collected in the
23 form of a methanol solution. Methanol was removed under reduced pressure, and the iDA
24 was characterized by FTIR and $^1\text{H-NMR}$ (Figure 1b-c). $^1\text{H-NMR}$ (D_2O): $\delta = 1.93 \text{ ppm}$ (s,
25 3H, CH_3), 2.81 ppm (t, 2H, $\text{CH}_2\text{-NH}_3$), 3.10 ppm (t, 2H, $\text{CH}_2\text{-CH}_2\text{-NH}_3$), 5.27 ppm (s, 1H,
26 $\text{CH}_2=\text{C}$), 5.78 ppm (s, 1H, $\text{CH}_2=\text{C}$), 6.72 ppm (m, 3H, aromatic).
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40 **2.3 Synthesis of the ionic hydrogels.** Hydrogels were synthesized by free radical
41 photopolymerization employing aqueous solutions of 50% w/v of the monomers. AAm,
42 HEA and METAC were used to co-polymerize with iDA at various monomer mixture
43 ratios (15%, 30% and 50% mol). SFMA was employed as a cross-linker/co-initiator and Rf
44 as the sensitizer, both at a concentration of 1% w/v in water taking into account monomers
45 mass.
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53 4 mL of the de-oxygenated pre-polymeric mixture was irradiated with constant stirring
54 for 3 h at room temperature in a home photoreactor composed of 12 blue light emitting
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3 diodes (LEDs) (λ^{\max} 455 nm). After irradiation, and following previous published
4 procedures,²⁷ reaction tubes were maintained for 48 h in the dark. Later, the hydrogel
5 products were removed from the tubes and cut into uniform discs of 10.5 mm in diameter
6 and 2.5 mm in thickness (~0.10 g). They were washed twice with MilliQ water for 5 h to
7 remove any unreacted species and finally dried in an oven at 40°C for 48 h.

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

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14 **2.4 Characterizations.** The new synthesized monomer and ionic hydrogels were
15 characterized by proton nuclear magnetic resonance (¹H-NMR), recorded in a Bruker
16 Avance 400 spectrometer operating at 400.15 MHz. Fourier transform infrared (FTIR)
17 spectra were recorded at room temperature with an Alpha Bruker- IR spectrometer applying
18 10 scans in transmission mode.

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21 Materials thermal properties were analyzed by differential scanning calorimetry (DSC)
22 performed on a DSC Q2000 differential calorimeter (TA Instruments). All the experiments
23 were performed under ultrapure nitrogen flow. The samples were heated at a rate of 20 K
24 min⁻¹, from - 50 °C to 100 °C.

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27 To visualize the internal structure and pore size of the hydrogels in the swollen state, a
28 JEOL JSM-6460 LV SEM (Scanning Electronic Microscopy), from Jeol Technics Ltd.,
29 Tokyo, Japan, was employed. The samples were swollen 15 h in simulated aquifer media at
30 25°C. Before SEM analysis, they were lyophilized to observe pore structure.²⁷

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33 **2.5 Swelling assays.** Dry discs of the hydrogels were weighted (W_0) and immersed in
34 simulated aquifer solution at 25°C. At established times, the samples were removed from
35 the simulated solution, externally dried with filter paper to eliminate excess of solution that

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3 could remain in the materials, and weighted (Wt).²⁷ The results were adjusted according to
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5 Equation 1.^{30, 31}

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

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10 Where n_p and K_p represent the swelling exponent and the kinetic constant of water
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12 diffusion into the network.²⁷

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15 **2.6 Pollutant removal procedure.** Organic and inorganic pollutants were employed in a
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17 limited concentration established by the World Health Organization.³² Each pollutant was
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19 followed by UV-Vis spectrophotometer from the maximum absorption peak of the
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21 substance or from the employment of complexes for colorimetric detection. A calibration
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23 curve was built for each species. Measurements were realized at room temperature with a
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25 Perkin-Elmer UV/Vis Lambda 950 spectrometer
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29 For contaminants removal, a dried disc of hydrogel was submerged in 10 mL of
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31 simulated aquifer with a particular pollutant, thus, at certain consecutive times, 3 mL of the
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33 remain solution was analyzed by UV-Vis spectrophotometer, after that, solutions were
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35 returned to the original flask. The detection was carried out until 24-48 h. The adsorption
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37 capacity, q (mg of contaminant adsorbed per kilogram of dry hydrogel) of the polymers
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39 was calculated using Equation 2:
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$$q = \frac{(C_i - C_t)V}{m} \quad (2)$$

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46 Where C_i and C_t represent the initial concentration and the concentration at time t of the
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48 pollutant (mg mL^{-1}), respectively, V is the total volume of the contaminant solution (mL)
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50 (in contact with the hydrogel) and m is the polymer mass (Kg).
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3 **2.6.1 Kinetic study.** Lagergren model. A kinetic analysis of the pollutants removal was
4 performed employing the differential equation of the pseudo-first-order developed by
5 Lagergren:³³
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$$\frac{dq_e}{dt} = k(q_e - q_t) \quad (3)$$

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14 Where q_e and q_t refer to the amount of contaminant adsorbed (mg Kg^{-1}) per amount of
15 dried hydrogel at equilibrium and a given time (t , h). k is the rate constant of the pseudo-
16 first-order adsorption (h^{-1}). The integration of Equation 3 for the boundary conditions (from
17 $t=0$ and $q_t=0$ to t and q_t) throw the following equation:
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$$\ln \left(\frac{q_e}{q_e - q_t} \right) = k t \quad (4)$$

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27 Which is the integrated rate law for a pseudo-first-order reaction. k , the rate constant, can
28 be acquired from the slope of the straight-line plots of $\ln (q_e/(q_e - q_t))$ against t .
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34 **3. RESULTS AND DISCUSSION**

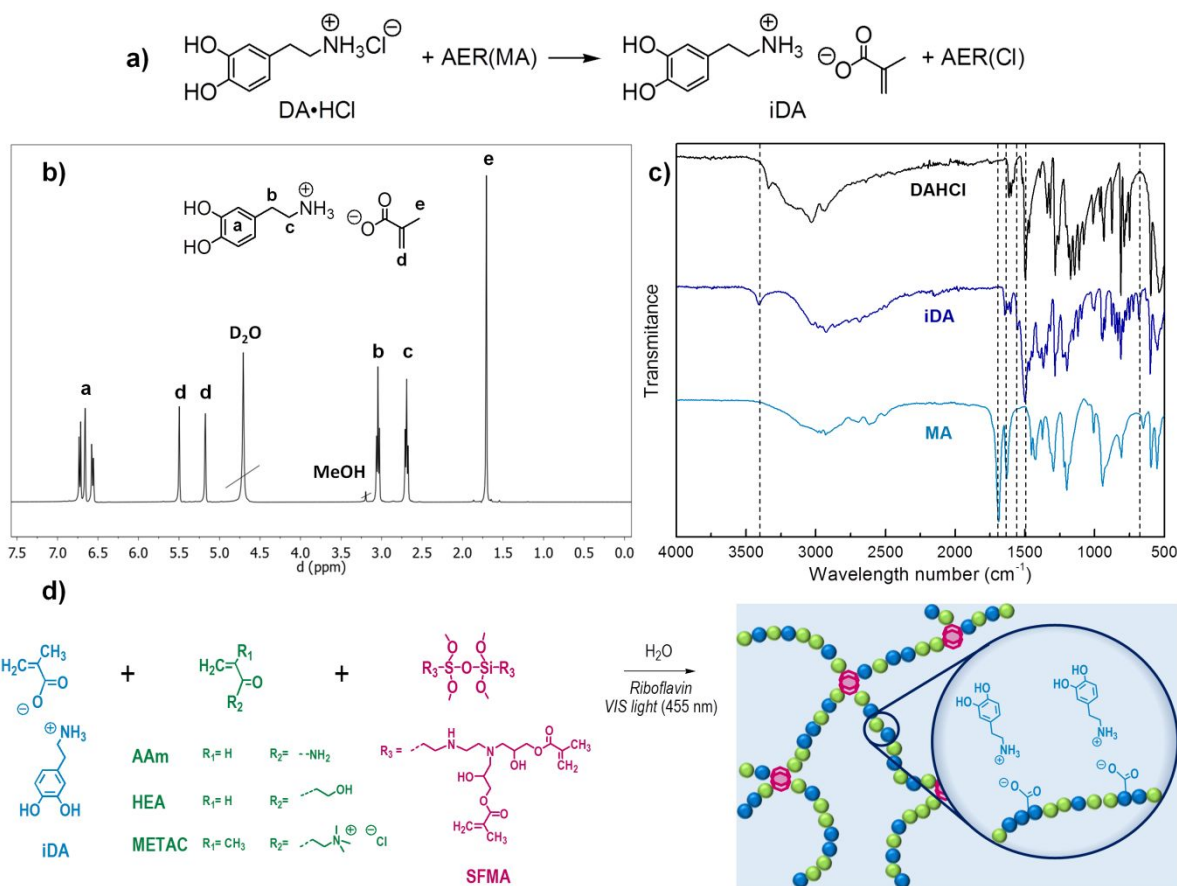
35 36 **3.1. Synthesis and characterization of catechol containing poly(ionic liquid)** 37 **hydrogels** 38 39

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41 The catechol-containing ionic monomer, dopamine methacrylic salt (iDA) was
42 synthesized using an ion exchange resin (AER) method from commercially available
43 dopamine hydrochloride (DAHCl). A methanol solution of DAHCl was passed through a
44 chromatographic column loaded with the AER resulting in the exchange of the chloride ion
45 for the deprotonated form of methacrylic acid as shown in Figure 1a. This simple AER
46 method produced a highly pure ionic monomer in a nearly quantitative yield (>90%
47 determined gravimetrically, with chloride content lower than 20 ppm, determined by the
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3 Silver chromate test).³⁴ The product was recovered in the form of a white solid readily
4 soluble in water. iDA structure was confirmed by FTIR and ¹H-NMR. Resonance peaks of
5 different protons in the synthesized monomer are assigned in Figure 1b. Figure 1c shows
6 the characteristic peaks of the new ionic monomer, iDA, and their starting reagents, DAHCl
7 and MA: the presence of the signal at 1632 and 651 cm⁻¹ corresponds to the vinyl group
8 from the acid (s; ν_s (C=C vinyl); (m; ν_s (=C-H vinyl)), these signals remain in iDA since the
9 methacrylate group is not affected during the synthesis. The signal at 1690 cm⁻¹, in MA
10 spectrum, corresponds to the stretching vibration of the carboxylic group (s; ν_s (C=O)) that
11 disappears in the spectrum of iDA due to the higher conjugation given by the carboxylate
12 group (m; ν_s (C=O)₂) that appears now at 1553 cm⁻¹. There are also some characteristics
13 bands of DAHCl present in iDA spectrum: the signal at 1500 cm⁻¹ due to the ring stretching
14 (m; ν_s (C=C arom.)) and the signals at 1583 cm⁻¹ and 3405 cm⁻¹ that belong to primary
15 amines bending and stretching modes.
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33 Next, iDA was employed to prepare hydrogels via visible light induced co-
34 polymerization with a series of water soluble (meth)acrylate based monomers, such as
35 HEA, AAm or METAC. SFMA, a synthesized functionalized silsesquioxane containing
36 amines and acrylates groups was employed as co-initiator and cross-linker.^{35, 36} Riboflavine
37 (Rf) was incorporated as a green visible light sensitizer for the photopolymerization process.
38 The reactions were carried out in water for 3 h with monomers concentration of 50 % w/v
39 (see scheme in Figure 1d). The chosen photoinitiator system avoids problems associated
40 with the presence of toxic aliphatic amines, in the final material, commonly employed as
41 co-initiators.³⁷ The reaction yield was high in all cases producing an insoluble fraction
42 (IF%) between 70 and 82 wt%, typical for this type of polymerizations. IF% represents the
43 percentage of polymer that is actually crosslinked in the hydrogel and was achieved
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3 gravimetrically through Soxhlet extraction with ultrapure THF during 24 h. Due to the
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5 good solubility of iDA in water, this photopolymerization procedure allowed to incorporate
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7 up to 50% wt of the ionic monomer in the hydrogel. The homopolymer of iDA couldn't be
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9 synthesized probably because the inhibition in polymerization reaction attributed to the
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11 presence of catechol groups. One of the risks of this synthetic pathway is that
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13 catecholamines can follow autopolymerization in aerated basic conditions, first
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15 demonstrated by Messersmith et al. for dopamine.³⁸ Following a multistep reaction
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17 pathway, dopamine can self-polymerize via radical polymerization and produce dark
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19 polymers which are usually complex networks with free catechol groups available for
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21 further chemical reactions.^{39, 40} In our case, the lack of brown color in the final hydrogel
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23 materials and the clean NMR signals could be assumed as a primary evidence of the
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25 absence of polydopamine.^{8, 41}
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32 **Figure 1.** (a) Scheme of ionic dopamine methacrylate (iDA) synthesis employing
33 dopamine hydrochloride and an anion exchange resin (AER); (b) $^1\text{H-NMR}$ spectrum of
34 iDA in D_2O and (c) FTIR of iDA, MA and DAHCl; (d) In-situ preparation of hydrogels
35 using *VIS* light polymerization, a functionalized silsesquioxane cross-linker (SFMA), ionic
36 dopamine methacrylate (iDA), and different (meth)acrylate monomers, acrylamide (AAm),
37 2-hydroxyethyl acrylate (HEA) or [2-(methacryloyloxy)ethyl] trimethylammonium
38 chloride (METAC) in the presence of Riboflavin in aqueous solution.

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40
41 Table 1 summarizes the composition and properties of hydrogels prepared with variable
42 ratios of iDA: HEA, AAm or METAC co-monomers. Hydrogels were characterized by
43 FTIR to confirm their chemical structure. Figure S1 shows the spectra of all co-polymers
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and homopolymers for HEA, AAm and METAC. Characteristics bands of the ionic monomer are observed in the catechol containing poly(ionic liquid) hydrogels.²⁵ Particularly, the characteristic transmittance between 3720 and 2375 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 cm^{-1} (s; ν_s (C=O)), 1161 cm^{-1} (s; ν_s (C-O)); PAAm at 1660 cm^{-1} (s; ν_s (C=O)), 1420 cm^{-1} (s; ν_s (C-N)); PMETAC at 1720 cm^{-1} (s; ν_s (C=O)), 500-550 cm^{-1} (s; ν_s (N-X₃⁺)), 1450-1480 cm^{-1} (s; ν_s (C-N)) were observed in the corresponding formulations.

The polymerization process was also followed by ¹H-NMR. Figure S2 shows that the polymer presents the regular spectrum of a crosslinked polymer showing very broad bands which make difficult to calculate the co-monomer composition. For this reason, other 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 _{max} (%)	n _p	R	T _g (°C)
HEA	0	94	353.0	0.49	0.99	2
P(HEA-co-iDA 15)	15	70	80.8	0.08	0.92	-4
P(HEA-co-iDA 30)	30	74	145.0	0.04	0.92	-14
P(HEA-co- iDA 50)	50	75	230.0	0.39	0.99	6
PAAm	0	96	797.0	0.45	0.99	81
P(AAm-co- iDA 15)	15	73	1974.0	0.67	0.99	3
P(AAm-co-iDA 30)	30	70	1838.0	0.65	0.99	6
P(AAm-co-iDA 50)	50	74	2298.0	0.85	0.99	11

PMETAC	0	98	2229.0	0.45	0.99	53
P(METAC-co-iDA 15)	15	82	2357.0	0.42	0.99	-7
P(METAC-co-iDA 30)	30	71	2242.0	0.48	0.96	-11
P(METAC-co-iDA 50)	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.^{30-31, 42} 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.^{43, 44} 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 rations less than 300% (see Table 1). Swelling results were fitted according to Equation 1. In Table 1 are

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3 summarized the diffusional exponent values, n_p , and the corresponding correlation
4 coefficient R. From the fitting, it can be highlighted that the correlation constant, close to 1,
5 is indicative of the good quality of the fitting. When the value of the exponent $n_p \leq 0.5$,
6 swelling follows Fick's law or is diffusional-controlled. Within experimental error, all
7 formulations follows a Fickian behavior while P(AAm-co-iDA) shows a non-Fickian
8 mechanism. The departure from Fick's law can be explained considering that the chains
9 relaxation rate is higher than the solvent diffusion rate in the hydrogel, which indicates the
10 presence of specific interactions (values of $n_p > 0.5$).
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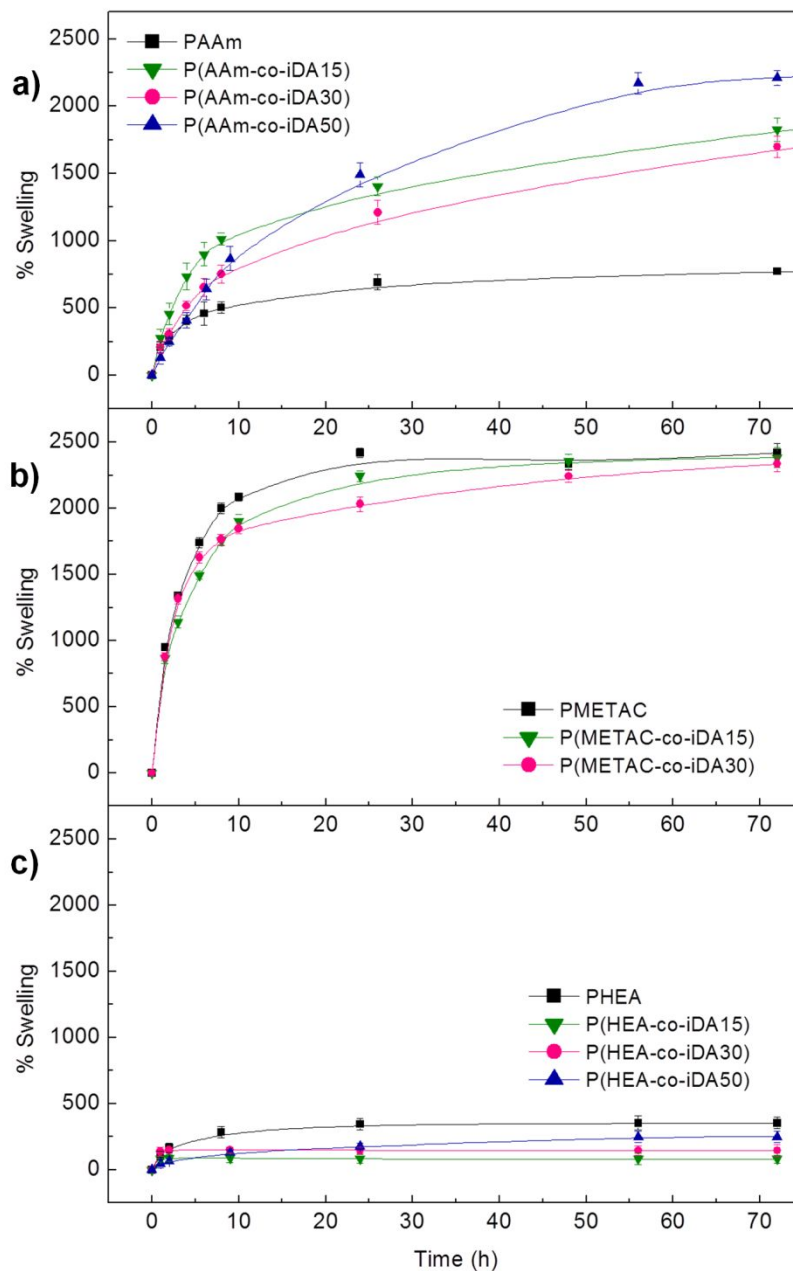


Figure 2. Swelling curves in simulated aquifer at 25°C for (a) PAAm and P(AAm-co-iDA) hydrogels; (b) PMETAC and P(METAC-co-iDA) hydrogels and (c) PHEA and P(HEA-co-iDA) hydrogels.

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3 Figure 3 shows SEM images of the internal structure of P(HEA-co-iDA15), P(AAm-co-
4 iDA15) and P(METAC-co-iDA15) lyophilized hydrogels, previously swollen in simulated
5 aquifer media for 15 h. The micrographs show that the average pore size changed
6 depending on the co-monomer when the amount of iDA was maintained constant. The
7 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
8 P(AAm-co-iDA15) and $4 \pm 2 \mu\text{m}$ for P(HEA-co-iDA15) hydrogels. The incorporation of
9 iDA into hydrogels also changed their internal structure. As an example, Figure S3 shows
10 micrographs of PAAm hydrogels, where the homopolymer displays smaller pores than the
11 co-polymer containing the ionic monomer. Next, Differential Scanning Calorimetry (DSC)
12 was employed to characterize dry hydrogels. Figure S4a shows DSC curves for HEA
13 hydrogels, where one single glass transition temperature at $2 \text{ }^\circ\text{C}$ was observed for the
14 homopolymer. When iDA was incorporated, T_g values decreased to $-4 \text{ }^\circ\text{C}$ for P(HEA-co-
15 iDA15) and $-14 \text{ }^\circ\text{C}$ for P(HEA-co-iDA30), but a broadening and an increase of T_g to $6 \text{ }^\circ\text{C}$
16 is observed finally for P(HEA-co-iDA50). This behavior was attributed to the mobility of
17 the chains that result from the competition between the steric effect associated with the
18 presence of a bulky group (more mobility) and the strong polar interactions established by
19 the ionic monomer group (less mobility).⁴⁵ At low concentrations of the ionic monomer, the
20 steric effect is dominant resulting in a decrease of T_g , whereas at high iDA concentrations
21 the polar interactions play a key role increasing T_g values. Similar trends were observed for
22 hydrogels containing AAm and METAC (see Table 1 and Figure S4b-c).
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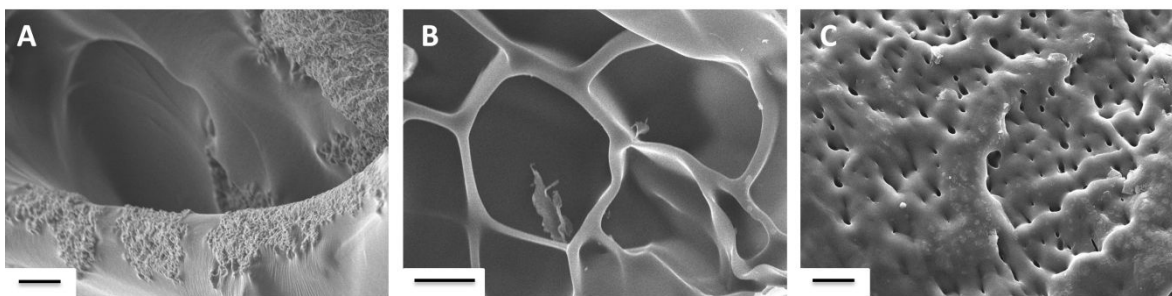


Figure 3. Scanning electron microscopy of lyophilized poly(ionic liquid) hydrogels, (A) P(METAC-co-iDA15), (B) P(AAm-co-iDA15) and (C) P(HEA-co-iDA15). Scale bar: 10 μm .

One potential drawback of the catechol/dopamine ionic functional hydrogels is the possible leaching of the dopamine cationic moiety which is linked by ionic interactions 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 π conjugation; this formation is accelerated at pH values above 6.^{8, 38} 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

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3 P(HEA-co-iDA50) hydrogel (as prepared before washing) was immersed in the simulated
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5 aquifer solution during 24 h to compare the spectra before and after the contact of the
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7 material with the aqueous solution. After the contact with the solvent, the hydrogel was
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9 dried at 48°C during 24 h. As confirmed by Figure S6, the spectrum taken after the assay
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11 kept the chemical structure and the same characteristics bands for the polymer composed of
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13 HEA and iDA. This result demonstrates the stability of the catechol moiety into the
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15 hydrogels.
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18 19 **3.2. Application of catechol containing poly(ionic liquid) hydrogels in water** 20 21 **purification** 22

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24 As a potential application, the pollutant removal capacity of catechol-containing
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26 poly(ionic liquid) hydrogels was tested to evaluate their potential use in water purification
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28 systems. The synthesized hydrogels were immersed into a series of simulated aquifer
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30 solutions, each of them containing the following pollutants: the organic anionic dye Eosin
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32 Y (EoY), organic cationic dyes like Methylene blue (MB) and Safranin (Saf), and heavy
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34 metals like Cu^{+2} and Co^{+2} and the oxoanions of As(V) and Cr(VI). Preliminary tests in
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36 simulated aquifer solutions containing concentrations of contaminants 100 times higher
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38 than the allowed values showed that the solutions became completely colorless after 6
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40 hours, while the color is retained into the hydrogels (Figure 4a).
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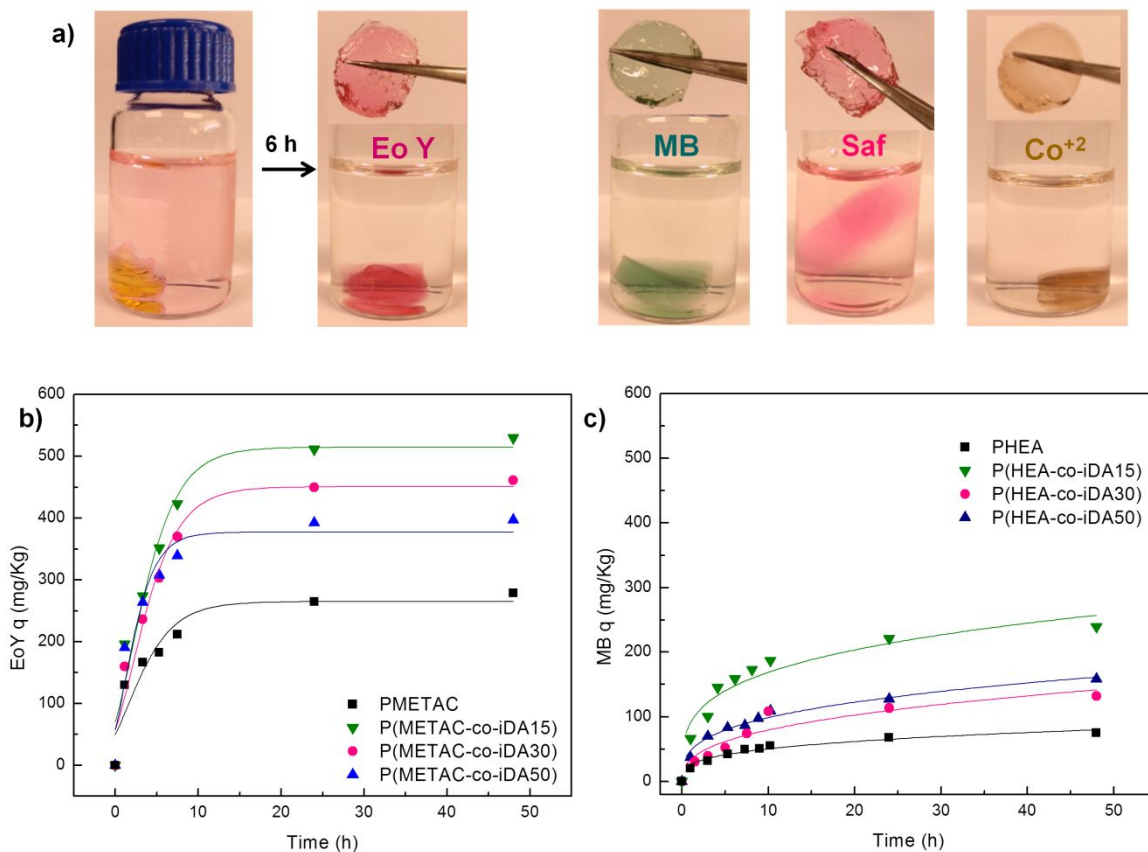


Figure 4. (a) Upper: photographs of different contaminants solution before and after 6 h of contact with P(HEA-co-iDA30), Eosin Y (EoY), Methylene Blue (MB), Safranin (Saf) and Cobalt salt (Co^{+2}); (b) Removal kinetics of EoY from P(METAC-co-iDA) hydrogels; (c) Removal kinetics of methylene blue (MB) 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 $[\text{EoY}] = 0.0025 \text{ mg mL}^{-1}$, $[\text{MB}] = 0.01 \text{ mg mL}^{-1}$, $[\text{Cr(VI)}] = 0.002 \text{ mg mL}^{-1}$ and $[\text{As(V)}] = 0.13 \text{ mg mL}^{-1}$. In all cases, 10 mL of solution were incubated with a $\sim 10 \text{ mg}$ 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

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3 without hydrogels were also performed to assess the stability of contaminants solutions.
4
5 Table 2 and Table S1 collect the experimental results expressed as q (capacity of pollutants
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7 removal established per unit mass of hydrogels - Equation 2). To qualitatively describe the
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9 adsorption process, the experimental data were fitted by pseudo-first-order kinetic model,
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11 known as Lagergren kinetic rate equation on adsorption processes (Equation 4).³³ The
12
13 following conclusions can be drawn from analysis of the results shown in Table S1. As
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15 expected, hydrogels containing METAC and AAm do not adsorb MB and EoY
16
17 respectively. This is presumably due to the predominant role that electrostatic repulsive
18
19 forces play in these systems and the fact that MB/METAC and EoY/AAm pairs are
20
21 positively and negatively charged under the experimental conditions. METAC groups are
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23 positively charged in P(METAC-co-iDA) hydrogels at pH 6, whereas AAm could be
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25 partially hydrolyzed as carboxylate groups,³⁵ because of the presence of catecholamines.
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27 This could be the explanation for the negative results, even though it is important to take
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29 into account that interactions between organic dyes and sorbents are complexes and not
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31 always directly related with electrostatic interactions.^{46, 47} For positive results, it is worth to
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33 remark that most iDA containing hydrogels show a higher dye removal capacity than their
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35 respective homopolymers. The dye removal capacity (at equilibrium) of iDA containing
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37 hydrogels is not directly proportional to the amount of iDA. This can be rationalized
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39 considering the different swelling properties of hydrogels and a number of interactions such
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41 as Van der Waals, hydrogen-bonding, and electrostatic forces play a role in the contaminant
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43 adsorption process. MB q values for our gels are similar to those reported for P(AAm-co-
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45 MMA) whereas EoY q values are higher than those reported by Milli et.al.^{48, 49} Adsorption
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47 time is an important parameter in any removal processes. Thus, kinetic studies in simulated
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49 aquifer solution at 25°C were performed for EoY and MB (Figure 4b-c and Table S1). High
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3 initial adsorption rates were observed for MB and EoY and both dyes were completely
4 removed after 5 h for most gels under the experimental conditions. Pseudo first order
5 kinetic constants (k) for dye adsorption by HEA based hydrogels are not affected by the
6 presence of iDA, whereas k values for AAm and METAC hydrogels containing iDA are
7 higher than that of the corresponding homopolymers. Reusability assays are planned to be
8 developed in future works, however some preliminary experiments were carried out for Eo
9 Y and MB. Both dyes are desorbed in a 60% in 4 h, nearly, from P(HEA-co-iDA15)
10 hydrogels in methanol, which may indicate the possibility of reusability of these materials.
11 Qualitative results are shown in Figure S7.
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24 Interestingly, the iDA containing hydrogels showed excellent results in the cases of
25 pollutant metal ions such as As(V) and Cr(VI) (Figure 5a-b). Removal kinetics for the
26 adsorption of As(V) and Cr(VI) are summarized in Table 2. As it can be seen, q values
27 increase with increasing the amount of iDA co-polymers for both heavy metal ions. Kinetic
28 profiles (in METAC and HEA based hydrogels) for As(V) removal and gel swelling are
29 similar, suggesting that the speed of heavy metal adsorption is in part limited by the gel
30 swelling process. It is worth to remark that these q values are compared favorably with the
31 highest performing hydrogels in the literature based on lays and chitin based hydrogels.
32 Catechol containing poly(ionic liquid) hydrogels benefit from the outstanding metal
33 chelating ability of catechols groups showing a great potential for heavy metal removal^{50, 51}
34 and preserving their ability to remove organic compounds with different charge.
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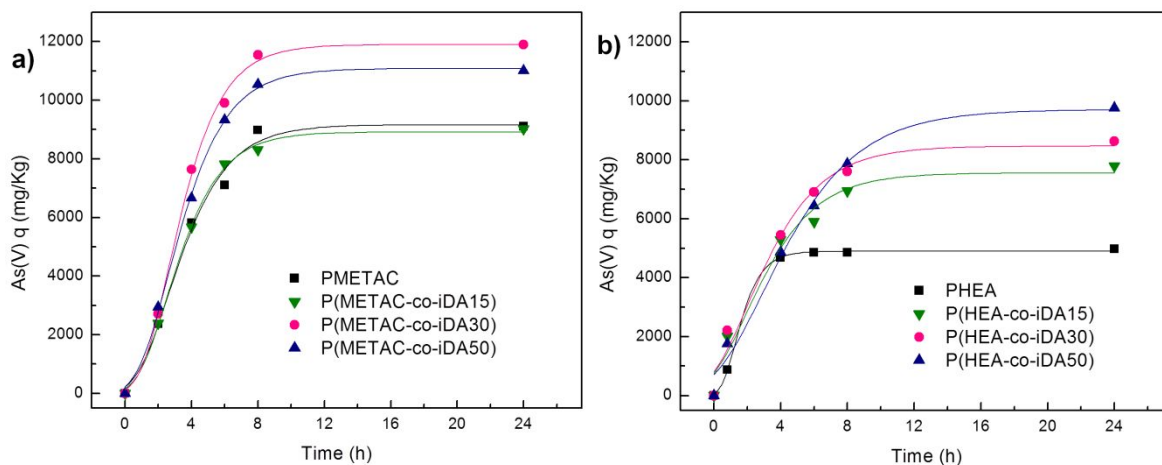


Figure 5. (a) Removal kinetics of As(V) from P(METAC-co-iDA) hydrogels; (b) Removal kinetics of As(V) from P(HEA-co-iDA) hydrogels.

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

Hydrogel	q As(V) (λ^{\max} 880 nm) (mg Kg ⁻¹)	k (h ⁻¹)	R	q Cr(VI) (λ^{\max} 540 nm) (mg Kg ⁻¹)
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. CONCLUSIONS

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 hydrophilic 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 homopolymers. 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. In summary, this paper displays 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. $^1\text{H-NMR}$ spectrum of the pre-polymeric solution and the polymerized hydrogel of P(HEA-co-iDA15) are included. Also,

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3 FTIR analysis and pictures for the leaching assays are presented. Finally, some pictures for
4 a potential reusability development are showed. This material is available on the Web at
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7 <http://pubs.acs.org>.

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8 9 Notes

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11 The authors have no competing financial interests.
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