

Micelle-Laden Hydrogel Microparticles for the Removal of Hydrophobic Micropollutants from Water

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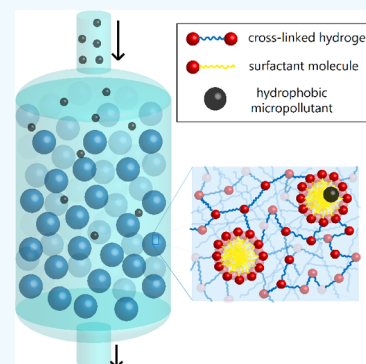
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ABSTRACT: Micropollutants, which occur at low concentration in the environment, are ubiquitous, hazardous, and difficult to remove from water by using current methods. This work introduces hydrogel-based polymeric absorbents containing immobilized micelles for the removal of hydrophobic micropollutants from water. Acrylated surfactants are synthesized and self-assemble into micelles with hydrophobic cores. The acrylate groups enable the incorporation of micelles into poly(ethylene glycol) diacrylate (PEGDA) hydrogels by free radical polymerization. NMR spectroscopy is used to characterize the cross-linked hydrogels. The hydrogels are formulated into microparticles by using droplet-based microfluidics to speed uptake by increasing surface area. Hydrophobic micropollutants quickly partition into the immobilized micelles within these microparticles, with mass transfer coefficients greater than those determined for a commercially available activated carbon that is frequently used for water purification. Finally, a sustainable and facile method of regenerating spent absorbent is demonstrated.

KEYWORDS: micropollutants, hydrogels, microparticles, micelles, water purification, separations



1. INTRODUCTION

Water is essential for human life and integral to sustainable economic development.^{1–3} Pollutants may be classified into two categories: macropollutants and micropollutants. Macropollutants are few in number but contribute to the bulk of water pollution; they include coliforms and other microorganisms, runoff from agriculture including phosphates and nitrates, and other organic matter. Micropollutants, on the other hand, are numerous, with each specific component contributing little to water pollution in terms of mass. Micropollutants include industrial organic solvents, intermediates and lubricants, industrial surfactants, household products such as detergents and disinfectants, antibiotics and other medications, certain heavy metals, food additives and flavoring agents, and nanomaterials.^{4,5}

Though their concentrations are low (~ 0.01 – $100 \mu\text{g/L}$), micropollutants have been detected to be prevalent in the environment based on the limited measurements that have been conducted.^{6–18} Disconcertingly, many micropollutants can have significant adverse effects on the ecosystem even in low concentrations, which has made them a problem of concern along with conventional macropollutants.^{2,3,11,12,19–26} Despite increased interest and the pressing need to develop technologies that can remove micropollutants from water, there has been little innovation in terms of new technologies.^{4,5,27} Because the problem of micropollutants has become apparent only relatively recently, most work on eliminating micropollutants has focused on technologies developed for the elimination of macropollutants, such as activated carbon

adsorption, ozone or peroxide oxidation, and photodegradation.^{4,5,11,13,28,29} Though many pharmaceuticals are effectively removed through biological treatment and photodegradation,^{14,30} the elimination of other micropollutants in wastewater treatment plants remains highly variable and is usually low.^{15–17,28,31,32} It is necessary to use multiple techniques sequentially to achieve removal,^{33,34} though even combined treatment strategies fail to eliminate molecules like ciprofloxacin.³⁵ There are additional well-known drawbacks to current methods. For instance, it is not environmentally sustainable to make activated carbon, and regeneration requires extremely high temperatures ($\sim 1000 \text{ }^\circ\text{C}$).^{33,36,37} Ozone or peroxide treatment may produce transformation products like chlorates and bromates, which may themselves be hazardous.^{38,39} Another classical technology known to effectively eliminate many pollutants is reverse osmosis, which shows poor elimination of hydrophobic micropollutants.^{40,41} Technologies designed for separating macropollutants are therefore not suited to the elimination of micropollutants. The United Nations Sustainable Development Goals⁴² seek to “ensure availability and sustainable management of water and sanitation for all”. It is apparent that this

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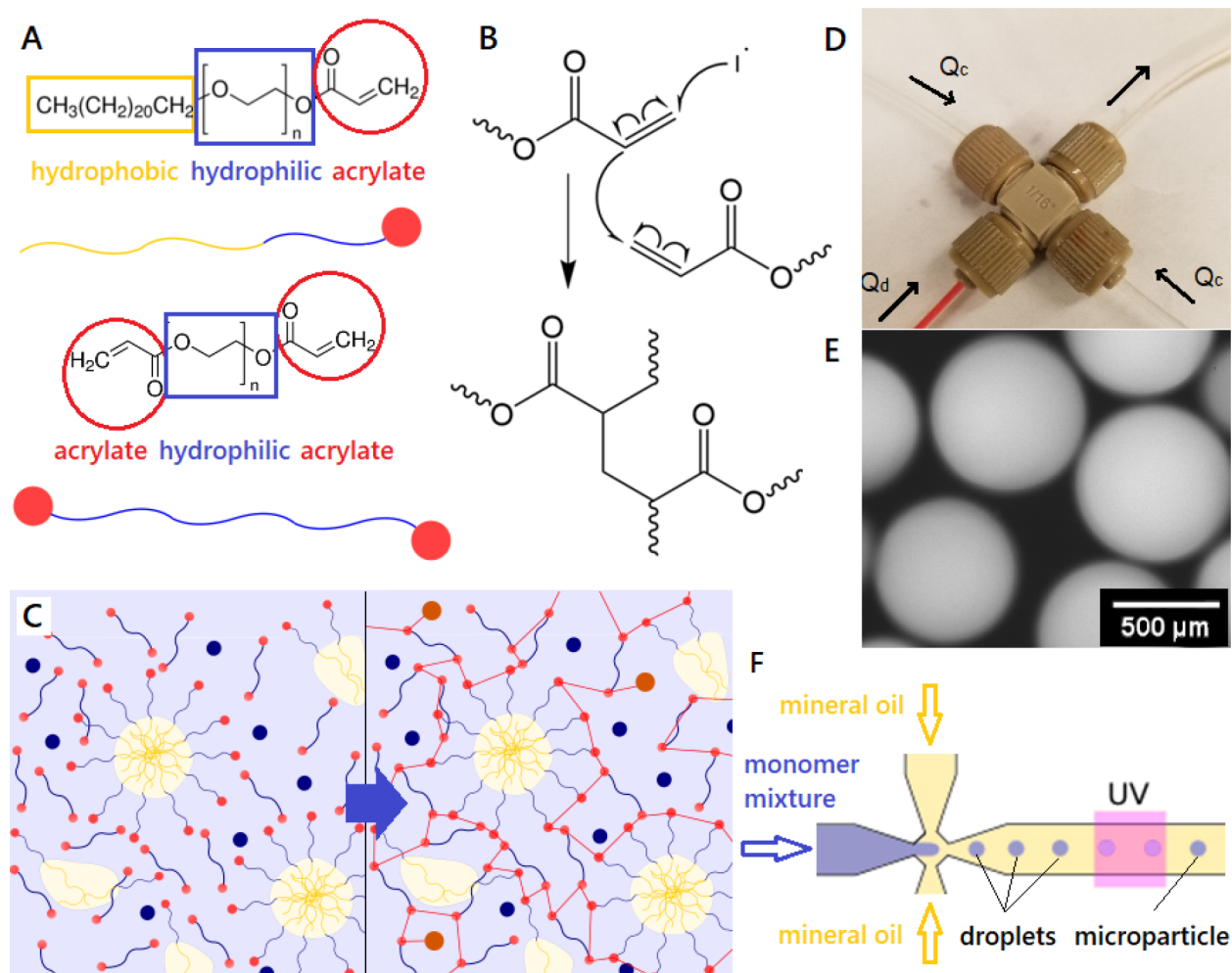


Figure 1. Synthesis of micelle-laden hydrogel microparticles. (A) Structural templates of the constituent surfactants and cross-linking agent. (B) Chain-growth polymerization of monomers to produce cross-linked bond network. (C) Surfactants form micelles in the monomer mix and are incorporated in this form into the cross-linked gel. (D) An off-the-shelf microcross used to process the monomer solution into droplets, which are then UV-polymerized into particles (E). (F) Schematic of the microcross and microparticle synthesis process.

goal will not be achieved without the development of technologies tailored to the removal of emerging contaminants from water.

There has been some nascent research into technologies specifically tailored to removing micropollutants from water based on absorbing polymers.^{27,43,44} There has also been interest in employing nanomaterials for the treatment of water.^{45,46} However, very few technologies have translated from the lab to implementation.^{47–51}

Micelles with hydrophilic shells and hydrophobic cores can be used to capture hydrophobic molecules from water.^{52,53} Micelle cores capture hydrophobic molecules into aggregates larger than the molecules themselves. These aggregates can be removed by using methods such as ultrafiltration that are easier to implement and more effective than reverse osmosis.^{40,41,54–56} Previous studies that attach micelles to much larger clay^{57,58} or magnetic particles⁵⁹ evade the extra ultrafiltration step. Here we report the synthesis of hydrogel microparticles containing chemically anchored micelles and demonstrate their use in water purification. In contrast with previous work that used surface adsorbents, these particles are bulk adsorbents and can therefore be larger and easier to separate from water (since surface area considerations are less important). They also have greater chemical diversity, show

faster uptake, are significantly easier to produce at scale, and are much easier to regenerate.

Though they are large enough to easily separate them from water (for example, by gravitational settling for a few seconds), microparticles are sufficiently small to limit the length scales on which transport needs to occur, allowing fast uptake. Microparticles can easily be made by using off-the-shelf devices like microcrosses, capillary devices, or T-junctions which are built from a few simple parts like tubes and adapters.^{60,61} Similar to previous work, we use a microcross with an aqueous phase flowing into a continuously flowing oil phase, resulting in droplet formation at the junction by pinch-off.⁶² Such devices are easy to build and scale up and produce monodisperse droplets with uniform sizes in a reproducible manner.^{62,63} Hydrogel monomers, micelles, and a photoinitiator are dissolved in the aqueous phase, and the droplets are UV-polymerized to create hydrogel particles. These hydrogel particles can be incorporated into existing unit operations like packed and fluidized beds for implementation in water treatment.

The partitioning of hydrophobic molecules into the micelle cores within the hydrogels is energetically favorable but does not result in the formation of strong physical or chemical bonds like in commercial activated carbon; this allows easy

regeneration of micelle systems. Here we introduce simple regeneration by washing with 90% ethanol. Ethanol is biosafe at low concentrations, inexpensive, and combustible, allowing for safe and economically productive disposal. Hydrophobic micropollutants are significantly more soluble in ethanol than water; only a small volume of ethanol needs to be used to regenerate hydrogel absorbent used to clean a large volume of water ($1:10^3$ – 10^9).

We also systematically compare our hydrogel materials with Brita activated carbon (AC), a commonly used activated carbon in water purification. Brita AC is a representative AC, which remains the only class of commercial methods used to remove micropollutants today, and has been used as a standard for comparisons in prior work.²⁷ We demonstrate that our materials not only solve the sustainability and regeneration concerns surrounding the use of activated carbon but also represent a scientific advance as a bulk-active replacement for surface-active activated carbon.

2. MATERIALS AND METHODS

2.1. Materials. All chemicals used in this study are purchased from Sigma-Aldrich and used as received. Materials used in hydrogel synthesis include PEGDA, PI, and surfactants. B2SMA is purchased from Sigma-Aldrich while S80TA, T80TA, and F127DA are synthesized from unacrylated precursors which are commercially available. Acryloyl chloride, dichloromethane (DCM), and sodium bicarbonate are used in the acrylation process, and 2-naphthol is used in uptake studies. Ethanol, used for regeneration, is purchased at 99.9% purity and diluted to 90%.

2.2. Synthesis of Acrylated Surfactants. Unacrylated precursors S80, T80, and F127 terminate in alcohol groups. Acrylate groups are attached following a modified form of the procedure described in prior studies.^{64,65} Surfactants are dissolved in DCM (120 mL), and a 20% molar excess of sodium bicarbonate is added. The same molar excess of acryloyl chloride is dissolved in DCM (20 mL), and the solution is added to the reaction mixture dropwise over 60 min with constant stirring. The reaction is then allowed to proceed with continuous stirring in the dark for 48 h. The mixture is then filtered by using a Buchner funnel to remove solids, and the solvent is removed under vacuum at 30 °C. H NMR spectroscopy is used to confirm acrylation and calculate conversion (>90% in all cases, Figure S5).

2.3. Synthesis and Processing. We synthesize micelle-laden hydrogel particles from an aqueous solution of monomers containing a cross-linking agent (poly(ethylene glycol) diacrylate (PEGDA), $M_n = 700 \text{ g mol}^{-1}$), a photoinitiator (2-hydroxy-2-methylpropiophenone (PI)), and one of four acrylated surfactants (B2SMA = poly(ethylene glycol)behenyl ether methacrylate, $M_n \sim 1500 \text{ g mol}^{-1}$; S80TA = Span 80 triacrylate, $M_n \sim 591 \text{ g mol}^{-1}$; T80TA = Tween 80 triacrylate, $M_n \sim 1472 \text{ g mol}^{-1}$; F127DA = Pluronic F127 diacrylate, $M_n \sim 12700 \text{ g mol}^{-1}$). The surfactants are chosen to represent a broad diversity of sizes and structures. B2SMA is a polyethoxylated alkane, S80TA is a sorbitan ester, T80TA is a polyethoxylated sorbitan ester, and F127DA is a poloxamer.

All surfactants can be considered to have the general form shown in Figure 1A, with one or more acrylate head groups, one or more hydrophilic blocks, and a hydrophobic block. This is in contrast to PEGDA, which has two acrylate groups and a single hydrophilic section. The acrylate groups enable the copolymerization of the surfactants with PEGDA, as shown in Figure 1B. Polymerization is induced by free radicals generated from the photoinitiator by exposing the monomer solution to UV light and results in the formation of the cross-linked bond network in Figure 1B. The surfactants have low critical micelle concentrations (CMCs) as shown in the Supporting Information and always exceed their CMCs in the monomer solution.⁶⁴ The amphiphilic structure of the surfactants causes them to assemble into micelles in the monomer solution and are

subsequently incorporated as micelles into the cross-linked hydrogel (Figure 1C).

The aqueous monomer solution is amenable to various forms of processing. We use an off-the-shelf microcross (Figure 1D) to prepare monomer droplets which form due to pinching off by a mineral oil phase, as shown in Figure 1E. These monomer droplets are then UV-polymerized to make hydrogel microparticles. Flow rates are tuned to make particles $\sim 500 \mu\text{m}$ in diameter, irrespective of particle composition. The resultant microparticles are stable in water for long periods of time (Figure S1). Figure 1E shows a fluorescence microscopy image of monodisperse particles incorporating PEGDA, B2SMA, and rhodamine acrylate made by this method, showing uniform cross-linking.

Cross-linked hydrogels so prepared are then washed over 7 days in water, which is replaced daily, to remove any unreacted monomers and oligomers that are not incorporated into the gel matrix. Extensive washing ensures that no hydrogel leaches into the water when used for micropollutant removal and enables detection and quantification of micropollutants at environmentally relevant concentrations. The entire synthesis process is summarized in Figure S2.

2.4. H NMR Spectroscopy for Characterization. All H NMR spectra were obtained by using a three-channel Bruker Avance Neo spectrometer operating at 500.34 MHz. The system is equipped with a 5 mm liquid-nitrogen cooled Prodigy broad band observe (BBO) cryoprobe. Data are collected with 16 scans per sample.

2.5. Uptake and Regeneration.
2.5.1. Equilibrium Uptake Experiments. Hydrogels are prepared by using a monomer solution with a fixed amount of cross-linking agent (10% PEGDA) and photoinitiator (5% PI), but with a varying amount of surfactant to assess effects on micropollutant uptake. 2-Naphthol is used as a canonical hydrophobic micropollutant in this work. 2-Naphthol has been used in prior work as a model micropollutant and is itself an organic pollutant of concern, known to be difficult to remove by using conventional methods.^{27,66} Varying quantities of 2-naphthol are dissolved in two solvents, water and 90% ethanol, and a known volume of hydrogel microparticles is added to each sample and mixed for 24 h in the dark. The initial concentration of 2-naphthol is low and in the range relevant to water purification. 2-Naphthol is detected by UV/vis absorbance spectroscopy using a spectrophotometer. Peaks in the spectrum at 273 and 326 nm are used to prepare a calibration based on the Beer–Lambert law, and accurate detection of micromolar concentrations is possible (Figure S3). The concentration of 2-naphthol in the supernatant is measured at equilibrium, and a mass balance is used to determine the concentration inside the hydrogel microparticles.

2.5.2. Uptake–Regeneration Cycling. The hydrogel microparticles are denser than water and can be separated by simple gravitational settling. After reaching saturation in a water solution, the 2-naphthol containing water is removed, and 90% ethanol is added to the spent hydrogel particles to regenerate them. Particles are mixed with 90% ethanol in the dark for 24 h, followed by a second 24 h wash in clean water to remove any residual ethanol that may interfere in 2-naphthol quantification. 2-Naphthol containing water is then added, and equilibrium uptake is measured as discussed above. These uptake–regeneration cycles are continued to assess the impact of repeated regeneration on hydrogel performance.

3. RESULTS AND DISCUSSION

3.1. Characterization of Hydrogels. Hydrogels prepared as described in section 2.3 are characterized by using H NMR spectroscopy to study conversion during the polymerization process and assess the extent of leaching during the washing process. The hydrogels we synthesize are cross-linked and therefore not soluble in any solvent, which precludes direct H NMR analysis. We therefore hydrolyze the synthesized gels using a strong base, 1 M NaOH. Hydrolysis breaks the ester linkages in PEGDA and the surfactants, leaving behind a mixture of poly(ethylene glycol) (PEG), unacrylated surfac-

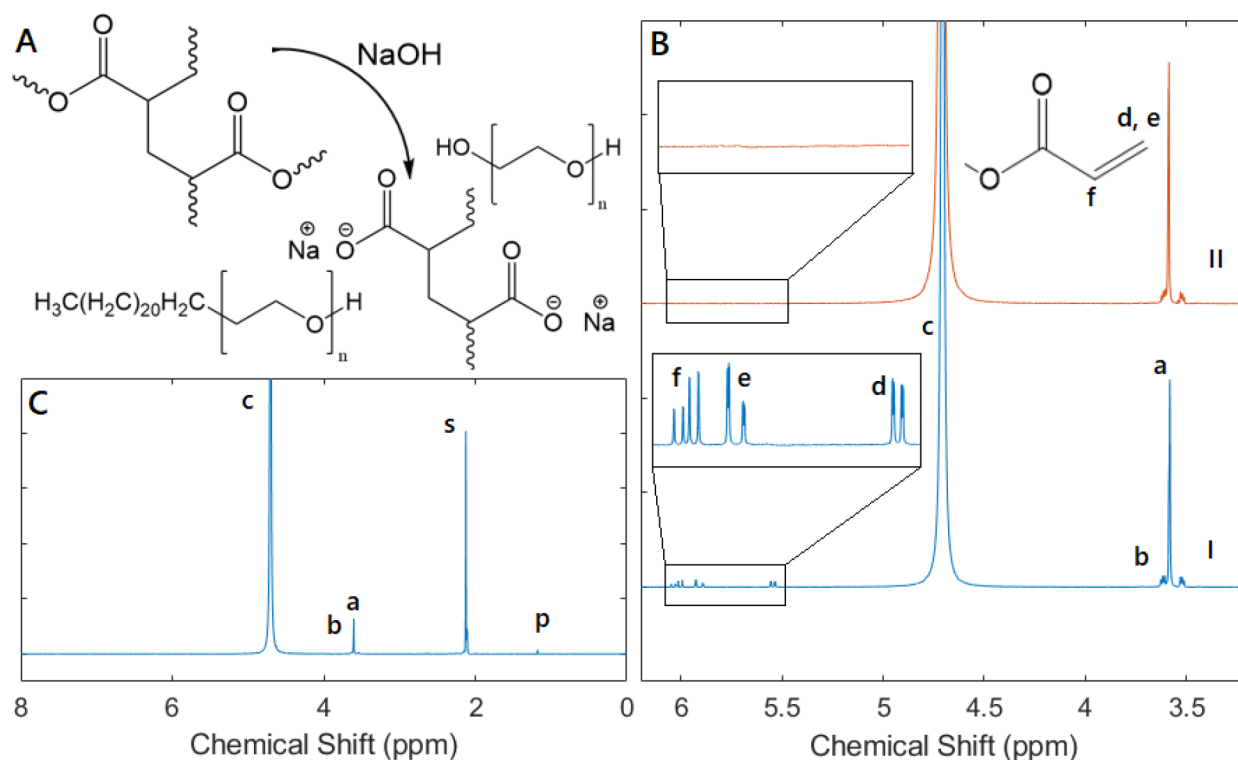


Figure 2. Conversion and incorporation of monomers in hydrogel microparticles: H NMR analysis. (A) Hydrolysis of hydrogels into soluble components for H NMR. (B) Spectra for the hydrolyzed monomer mixture (blue) and for hydrogels hydrolyzed immediately after polymerization (red). Any oligomers are removed through 7 days of washing, and cleaned hydrogels are hydrolyzed and analyzed to obtain (C), which also contains acetone as an internal standard.

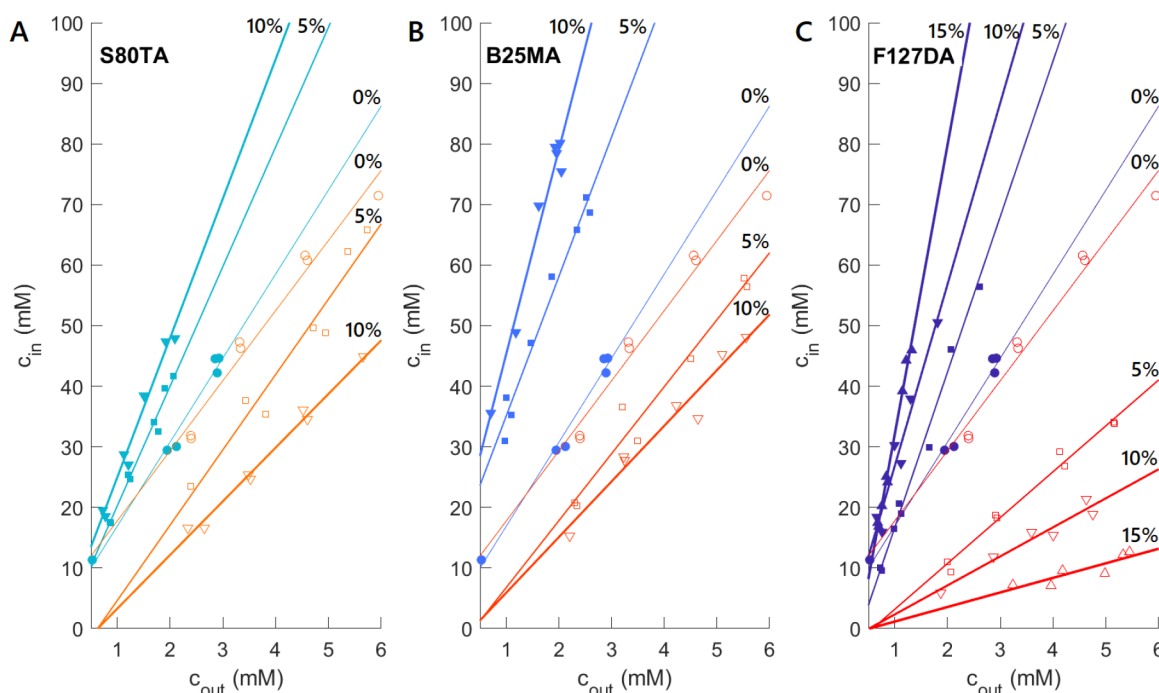


Figure 3. Equilibrium isotherms for the uptake of 2-naphthol dissolved in water (blue) and 90% ethanol (red). Isotherms are shown for three surfactants: (A) S80TA, (B) B25MA, and (C) F127DA, each with various concentrations. Note that the isotherms should not be interpreted to extend to very low concentrations, below 0.5 mM, which are outside the linear regime.

tant, and sodium polyacrylate, all of which are oligomers soluble in water (Figure 2A). This hydrolysis process does not affect any unreacted double bonds and can be used to analyze conversion.

Figure 2B shows H NMR spectra corresponding to the hydrolyzed monomer solution (I) and the hydrolyzed hydrogel particles (II) for a composition of 10% PEGDA, 5% PI, and no surfactant. Peaks a and b correspond to PEG protons, peak c to

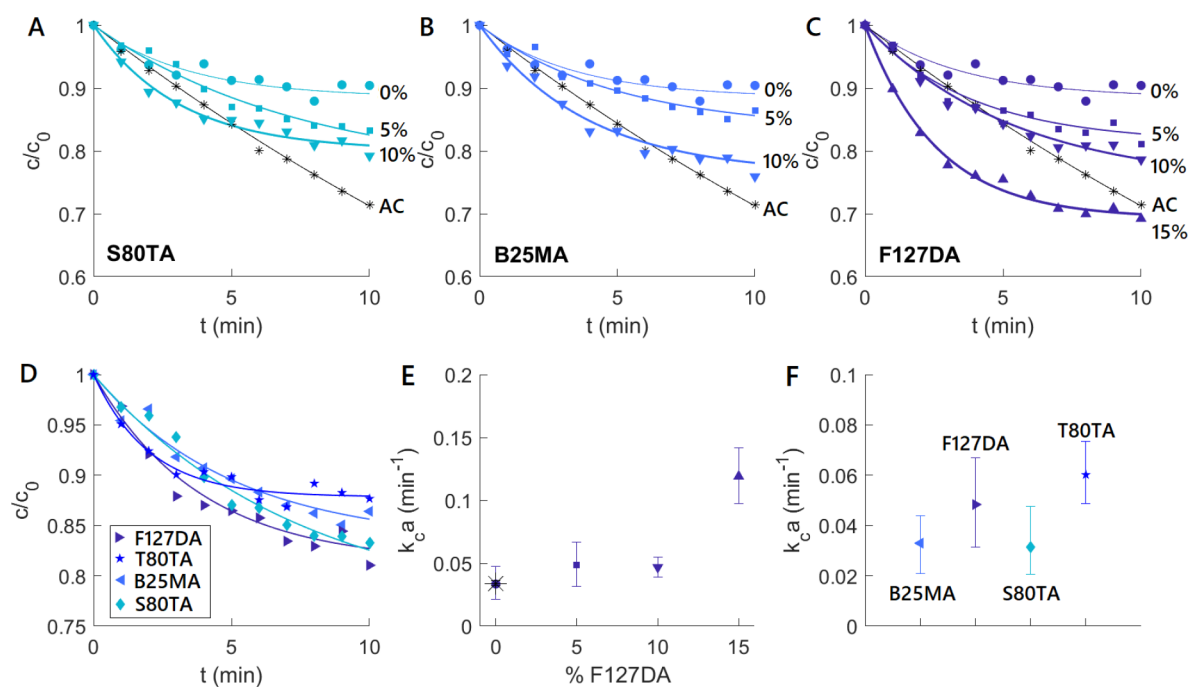


Figure 4. Pollutant removal kinetics. The concentration of 2-naphthol in the supernatant over time when removed by using hydrogel microparticles containing (A) B25MA, (B) F127DA, and (C) S80TA. Uptake by activated carbon shown by using black asterisks. (D) Comparison of profiles for four surfactants at the same concentration (5%), as a common point of comparison. (E, F) Mass transfer coefficients corresponding to the hydrogel microparticles and a commercial activated carbon (Brita AC; black asterisks).

protons in the solvent (water), and peaks d, e, and f to acrylate protons. The disappearance of peaks d, e, and f during the polymerization process indicates near-complete conversion of double bonds. However, not all molecules are incorporated into the gel matrix, with some forming oligomers held within the hydrogel by steric effects. These oligomers are slowly released into water during washing over the course of a week. The concentrations of such oligomers are sufficiently low as not to affect most hydrogel applications; in this study, we analyze them carefully because they could potentially interfere with the detection of low concentrations of micropollutants.

The amount of PEGDA and PI incorporated into the hydrogel particles can also be determined by using H NMR analysis. Figure 2C shows the H NMR spectrum corresponding to particles that are hydrolyzed after washing for 7 days to remove any unincorporated oligomers. Peaks a, b, and c are as described above, and peak p corresponds to the photoinitiator (PI). Peak s corresponds to acetone, a precise amount of which is added as an internal standard. An internal standard is essential to benchmark the decrease in the area of peaks a, b, and p compared to the original mixture (Figure 2B), while correcting for any measurement linked variation that may occur. Acetone is used as an internal standard because it is miscible with the hydrolyzed mixture because it produces only one sharp peak in H NMR spectra and because that peak is well-separated from other peaks of interest. Because the concentration of acetone is known, the area under the acetone peak can be used to determine the concentrations of PEGDA and photoinitiator. These are found to be lower than the concentrations in the unwashed particles (Figure 2B), and the difference corresponds to the loss of PEGDA and PI during the washing process, in the form of unincorporated oligomers. We determine the difference to be 18.8% of the initial amount of PEGDA and 62.1% of the initial quantity of PI, for a

composition of 10% PEGDA, 5% PI, and no surfactant. The amount of photoinitiator loss is much larger because the PI is in significant molar excess (molar ratio 4.43:1) to ensure fast polymerization and because smaller oligomers have a greater molar fraction of PI than PEGDA.

3.2. Equilibrium Uptake and Regeneration. Hydrogels are prepared by using a monomer solution in water with a fixed amount of cross-linking agent (10% PEGDA) and photoinitiator (5% PI), but with a varying amount of surfactant to assess effects on micropollutant uptake. The amount of surfactant is limited by solubility for B25MA, S80TA and T80TA but by the formation of a gel for F127DA. Varying quantities of 2-naphthol are dissolved in two solvents, water and 90% ethanol, and the initial concentration of 2-naphthol is in the range relevant to water purification. 2-Naphthol containing water is mixed with the hydrogel microparticles, and concentrations of 2-naphthol inside and outside the particles are recorded at equilibrium, as detailed previously. These data are then used to produce the equilibrium isotherms shown in Figure 3.

Straight lines can be seen to fit the data in Figure 3 well. The parameter of interest is the slope of the equilibrium isotherms, called the partition coefficient, defined here as the ratio of the concentration of 2-naphthol inside the particles to the concentration in the supernatant at equilibrium. The partition coefficient is greater than 1 for all systems, indicating that hydrophobic micropollutants always preferentially partition into the hydrogel microparticles. This partitioning is a combination of two effects: the physical separation of pollutant molecules into hydrophobic micelle cores and the formation of hydrogen bonds between the pollutant molecules and ethylene oxide units in the hydrogel matrix. The first effect is weakly dependent on the supernatant and is responsible for preferential partitioning in surfactant-free hydrogel micro-

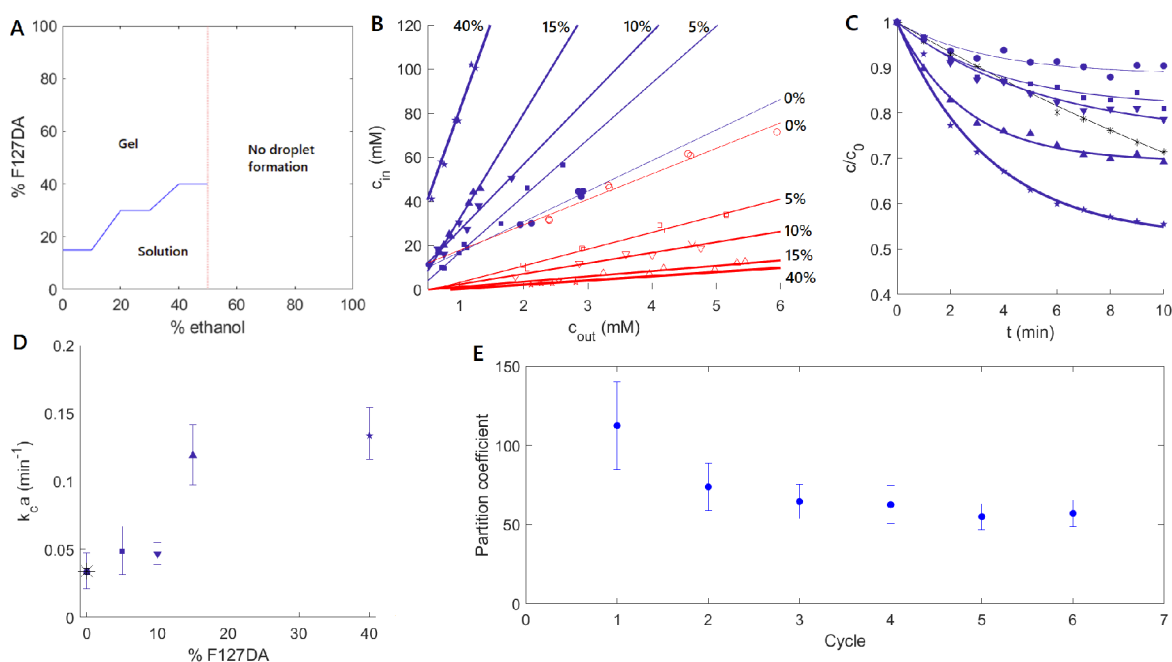


Figure 5. Effect of preparing F127DA monomer solutions in ethanol–water mixtures to boost surfactant incorporation. (A) Phase diagram showing the sol–gel transition in F127DA systems with 10% PEGDA, 5% PI dissolved in ethanol–water mixtures, and the domain in which surface tension allows good quality droplets to form. (B) Equilibrium isotherms corresponding to the 40% F127DA in 40% ethanol system compared to F127DA systems in water. (C) Kinetics and (D) mass transfer coefficients showing the same comparison and also comparing performance with a commercial activated carbon (Brita AC). (E) Partition coefficients for the 10% PEGDA, 5% PI, 40% F127DA system in water across multiple uptake–regeneration cycles.

particles. The second, micelle-mediated effect is strongly dependent on the supernatant; hydrophobic molecules prefer micelle cores to water, but this preference is much lower when the supernatant is itself more hydrophobic.

We therefore observe that the partition coefficient when water is the supernatant increases upon increasing the amount of surfactant in the hydrogel; the increase is attributed to the increased number of micelles in the hydrogel, increasing its carrying capacity. The introduction of micelles disrupts hydrogen bonding in the hydrogel, but the micelle-mediated effects dominate when water is the solvent. F127DA has higher partition coefficients than S80TA and B25MA, corresponding to the larger size of the hydrophobic zone in those molecules.

On the other hand, the micelle-mediated effect is weaker and does not dominate when the supernatant is 90% ethanol, which has greater affinity for hydrophobic molecules than water. The disruption of hydrogen bond formation due to the introduction of micelles is now the dominant effect, and the partition coefficient decreases with an increase in surfactant concentration (red isotherms in Figure 3).

As expected, the partition coefficient is larger when water is the supernatant compared to ethanol, and this difference is leveraged to regenerate spent absorbent. Hydrogel microparticles are used to clean contaminated water, and pollutant can be recovered from microparticles by washing with a smaller volume of 90% ethanol. We used 90% ethanol because it is sufficiently hydrophobic, relatively inexpensive (being lower in concentration than the ethanol–water azeotrope), biocompatible in trace amounts (if it enters the water stream through regenerated particles), and flammable (so it can be used as a fuel or fuel additive, destroying any pollutant molecules during combustion).

3.3. Kinetics of Water Purification. The rate of pollutant removal is as important as the equilibrium capacity of the absorbent in water purification applications. Hydrogel microparticles ($500 \pm 75 \mu\text{m}$) are prepared by using a monomer solution with 10% PEGDA, 5% PI, and varying surfactant fractions. The microparticles are added to a well-mixed bath containing 100 times their volume of 5 mM 2-naphthol, and absorbance spectroscopy is used to track the concentration of 2-naphthol in the supernatant over time, which is shown in Figure 4.

Figures 4A–C show the decrease in 2-naphthol concentration in the supernatant over time, which corresponds to the uptake of pollutant molecules by the hydrogel microparticles in the bath. The decrease is exponential, and increasing the surfactant fraction in the microparticles increases the speed and extent of pollutant removal. All micelle-laden hydrogels perform better than hydrogels without surfactants (shown by using filled circles). We compare the performance of these materials to an equal weight of commercial activated carbon sold to clean drinking water (Brita AC, in black asterisks). One of the formulations shown here, with 15% F127DA, can be seen to outperform an equal mass of activated carbon in terms of total pollutant removed on the short time scales that are more relevant to water purification, where contact times are typically on the order of minutes.⁶⁷ Additional data for longer time scales are shown in Figure S6 for interested readers. Figure 4D indicates that there is slight variation across surfactants at the same concentration, with F127DA-containing particles showing the best performance. The concentration (5%) is chosen as a common point of comparison, and data over a range of concentrations are shown in Figure S7 for the interested reader.

The data in Figures 4A–D fit eq 1, which is derived in the Supporting Information.

$$\frac{c(t)}{c_0} = \frac{\frac{V}{V_p K} + e^{-(1+V/(V_p K))k_c a t}}{1 + \frac{V}{V_p K}} \quad (1)$$

Here, V is the bath volume, V_p is the absorbent/adsorbent volume, K is the partition coefficient defined in the previous section, and $k_c a$ is the mass transfer coefficient. The mass transfer coefficient is the parameter of interest in water purification studies because it limits the maximum water flow rate through the absorbent bed. The mass transfer coefficient increases with increase in surfactant present within the hydrogel (Figure 4E) and is larger than the mass transfer coefficients corresponding to surfactant-free hydrogels and activated carbon. F127DA- and T80TA-containing hydrogels have a higher mass transfer coefficient than B25MA- and S80TA-containing hydrogels; this corresponds to the larger hydrophobic groups in F127DA and T80TA compared to B25MA and S80TA.

3.4. Nonaqueous Solvents to Increase Surfactant Load. The extent and speed of pollutant uptake increase with surfactant concentration, which is limited by solubility for B25MA, S80TA, and T80TA and by the formation of a gel for F127DA. Gelation precludes the use of a microcross to prepare droplets and also prevents polymerization due to the high viscosity of the sample. With 10% PEGDA and 5% PI, the concentration of F127DA cannot exceed 15% in the aqueous monomer solution without forming a gel. However, gel formation can be inhibited by dissolving the monomers in a mixture of water and ethanol. Phase equilibria in similar systems have been studied previously, and it is known that 30% or higher ethanol amounts allow the dissolution of greater amounts of F127 without gelation.⁶⁸ At the same time, ethanol concentrations cannot exceed 50% because this reduces the surface tension of the monomer solution to the extent that stable droplet formation is not easily achievable.

Figure 5A shows a phase diagram corresponding to a monomer solution with 10% PEGDA, 5% PI, and varying concentrations of F127DA dissolved in water–ethanol mixtures with varying ethanol fractions. The maximum F127DA concentration that can be achieved without gelation is 40%, when 40% of the solvent is ethanol. The presence of ethanol does not affect the uptake capacity of the microparticles significantly (Figure S4), and microparticles made from 10% PEGDA, 5% PI, and 40% F127DA in 60% water and 40% ethanol are expected to show the fastest and greatest pollutant uptake.

The equilibrium isotherm corresponding to the 40% F127DA/40% ethanol system is shown in Figure 5B. As before, the increase in surfactant load increases the water partition coefficient (to nearly double that of 15% F127DA particles) and reduces the ethanol partition coefficient. The speed and extent of uptake (Figure 5C) are also improved due to an increase in the mass transfer coefficient (Figure 5D). The total pollutant removed is twice the amount removed by activated carbon in 5 min, and 40% F127DA particles achieve the same amount of pollutant as an equal mass of activated carbon with a contact time of 10 min in only 3 min. The mass transfer coefficient is 4 times the commercial activated carbon. Note that the increase in mass transfer coefficient decreases with increasing F127DA loading. This is a result of two

competing effects: (i) greater number of micelles, which increase mass transfer, and (ii) denser (and less porous) particles, which lowers mass transfer.

Finally, Figure 5E shows partition coefficients for the 40% F127DA particles across multiple cycles of uptake and regeneration. Cycle 1 data are for uptake before the first regeneration step, cycle 2 data are for uptake before the second regeneration step, and so on. The initial decrease of about 34% corresponds to the formation of hydrogen bonds with the hydrogel backbone (since these bonds cannot be reversed by the addition of ethanol in the regeneration step) and provides additional support for the mechanism of uptake proposed above. After the modest decrease during the first cycle, the partition coefficient is seen to stabilize. Further decreases will occur on much longer time scales associated with particle breakdown, which can take several years at pH 7. The particles can therefore be used without further loss in performance over long periods of time.

4. CONCLUSIONS

We have demonstrated the use of micelle-laden hydrogels for the removal of hydrophobic micropollutants. We used a model hydrophobic micropollutant, 2-naphthol, in this study, but the approach extends to the removal of any hydrophobic micropollutant since it is not dependent on the formation of specific chemical bonds. Both the speed and extent of pollutant removal increase with the amount of surfactant incorporated into the hydrogels, and surfactants with larger hydrophobic segments are more effective in removing pollutant molecules. Preparing microparticles by using the hydrogels reduces the length scale of pollutant transport, and the materials studied in this work have higher mass transfer coefficients than a commercial activated carbon. The production of microparticles is easy to scale up. We also demonstrated that the presence of micelles allows spent absorbent to be regenerated, and the extent to which regeneration is possible increases with increase in the amount of incorporated surfactant. Finally, testing across multiple uptake–regeneration cycles demonstrates that these microparticles can be used for long periods of time without significant loss in performance. Micelle-laden hydrogel microparticles are therefore a promising material for the elimination of hard-to-remove hydrophobic micropollutants from water.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsapm.1c01691>.

Microscope images of synthesized microparticles, experimental schematics, absorbance spectra, Beer–Lambert calibration curves, effect of ethanol on equilibrium isotherms, H NMR spectra of acrylated surfactants, and derivation of the uptake kinetics equation (PDF)

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Notes

The authors declare no competing financial interest.

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