

Hydrogels of Versatile Size and Architecture for Effective Environmental Applications

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Cationic hydrogels from a positively charged monomer, (3-Acrylamidopropyl)-trimethylammonium chloride (APTMACl), were synthesized as bulk, and micro- and nano-sizes. These hydrogels were utilized to remove contaminants such as food dyes and an environmentally toxic metal, arsenic. The micro- and nanohydrogels were dispersed in another hydrogel network to design a semi-interpenetrating network (semi-IPN) which was shown to visualize the particles that can be used for absorption purposes. The micron-sized cationic hydrogel particles were very effective in the removal of arsenic from an aqueous environment- 96% of the arsenic was removed in less than 10 min from a 55-ppm aqueous stock solution. Cationic hydrogels ca. 5 nm were also prepared and demonstrated for fluorescein dye absorption in the nanohydrogel-hydrogel semi-IPN. Hydrogel particle sizes were investigated with microscopic methods, such as optical, fluorescence, scanning electron and transmission electron microscopes.

Key Words: Arsenic removal, environmental hydrogels, microgels, nanogel, nanotechnology, semi-IPN networks.

Introduction

As intriguing materials, hydrogels are smart, environmentally sensitive, and compatible with biological systems, and can be made responsive and degradable to various stimuli.^{1,2} Due to their 3-D networks of hydrophilic polymers imbibing large amounts of water, hydrogels are soft and elastic, and offer excellent properties for many applications.^{3,4} Their liquid-like and solid-like characteristics make hydrogels indispensable materials in aqueous environments as compared to conventional ones.⁵ Trevors and Pollack raised an interesting possibility, that the hydrogel environment could be superior to a liquid environment for the origin of life.⁶ Owing to their ability to change shape and volume in response to external stimuli, hydrogels have been studied intensively for a variety of applications, ranging from biology to the environment.⁷⁻⁹ Amongst hydrogel-forming materials, polyelectrolytes with ionizable groups have a special significance, since they insinuate network-responsive properties. Many applications of polyelectrolytes are due to their ability to bind oppositely charged species to form complexes. Most of the hydrogels used for metal ion removal have or are

able to develop negative charges to form complexes with positively charged metal ions.^{10–12} In the present work the syntheses of completely positively charged hydrogels in a variety of shapes, such as bulk, and micro- and nanosize, have been prepared and utilized for environmental applications. For micro- and nanohydrogel syntheses a water-in-oil micro-emulsion system was adopted. It was demonstrated that cationic hydrogels can successfully remove negatively charged species such as dyes and an important environment contaminant, arsenic, from aqueous media.

Arsenic is a persistent contaminant in underground and drinking water and its removal is of paramount importance. As a toxic and carcinogenic metalloid, arsenic removal poses a most challenging task due to its various oxidation states: pentavalent arsenate (As(V)), trivalent arsenite (As(III)) as cations, and trivalent arsine (As(III)) as anion. Furthermore, it can even have a zero valent as a semi-metallic elemental form, (As).^{13–16} Arsenic is labile and can have any of these chemical forms, depending on environmental factors. In that regard, use of environmentally sensitive hydrogels might offer a plausible solution for the concurrent removal of various forms of arsenic from aqueous environments. For example, hydrogels containing cationic and anionic charges can be prepared readily and simultaneously, used for the various oxidation states of arsenic. Additionally, different-sized hydrogel particles can be prepared for rapid removal. Particle size of hydrogel is one the most important factors for fast response time, which is the key factor in medical, sensor, and environmental applications. Smaller particles have a much higher interfacial area per unit mass of gel, endowing much greater exchange rates and can be readily packed in columns or embedded in another network.¹⁷ Therefore, in the current report, positively charged micron-sized hydrogel particles (microgels) were prepared and employed for the removal of arsenic from an aqueous environment. In fact, these microgels were very effective in removing 98% of the arsenic from an aqueous environment, 98% in less than 10 min. Moreover, ultra-small (~5 nm) particles of the same material were also prepared and embedded in another network, and were shown to be a very useful absorbent. For example, the removal of fluorescein dye from an aqueous environment was verified by these nanogel-embedded hydrogel networks (semi-IPN).

Experimental Methods

Chemicals

(3-Acrylamidopropyl)trimethylammonium chloride (APTMACl), and acrylamide (AAm) as monomers, N,N'-methylenebisacrylamide (MBA) as a crosslinker (X), ammonium persulfate (APS) and 2,2'-azobisisobutyronitrile (AIBN) as initiators, N,N,N',N'-tetramethylethylenediamine (TEMED) as an accelerator, L- α -phosphatidylcholine (lecithin) and dioctyl sulfosuccinate sodium salt (AOT) as surfactants, and cyclohexane and 2,2,4-trimethylpentane (isooctane) as solvents were used. All chemicals were products of Aldrich Chemical Company, Inc. (Milwaukee, Wisconsin). Fluorescein sodium salt (FSS), as fluorescent dye, was also used and purchased from Aldrich, while commercially available food dyes, such as FD&C Blue No. 1 (C₃₂H₃₄N₂N₂O₉), FD&C Red No. 3 (C₂₀H₆I₄Na₂O₅), and FD&C Yellow No. 5 (C₁₆H₉N₄Na₃O₉S₂), were obtained from a convenience store. Sodium hydrogen arsenate (Na₂HAsO₄·7H₂O), ACS, 98.0%-102.0% (Alfa-Aesar) was used as the source of As(V).

Bulk Hydrogel Preparation

The typical hydrogel of APTMACl preparation was as follows: 1 g of monomer and 0.5 ml of water containing the desired amount of X and 100 μ l TEMED was mixed thoroughly. To this solution was added 0.5 ml of 1% (by mole with respect to monomer) APS solution. After mixing completely, the obtained clear solution was injected into plastic straws of desired diameter and/or between 2 sealed glass slides, and kept for at least 24 h to complete the polymerization and crosslinking reaction at ambient temperature. Following cutting to the preferred size and shape (ca. 0.5×0.3 mm in diameter for cylindrical hydrogels, 1×1 cm for the disks, both ~ 0.75 cm in thickness), hydrogels were kept in distilled water for at least 5 days, replacing the water daily to remove any impurities, such as monomer, initiator, etc. With the UV-irradiation method for hydrogel preparation, the same procedure was employed, except that TEMED and APS were replaced by 50 mg of AIBN and the hydrogel precursor solution was irradiated in a photochemical reactor operating with 120 volts, 50/60 Hz (The Southern New England Ultraviolet Company, CT, USA. Model RPR-100).

Micro- and Nanohydrogel Synthesis

For micro particles of APTMACl hydrogels, lecithin micro-emulsion in cyclohexane was used, employing the UV-irradiation technique. The synthesis and characterization of the microgels were previously reported.¹⁸ The lecithin micro-emulsion was characterized by the water/lecithin molar ratio, W_0 ($W_0 = [\text{H}_2\text{O}]/[\text{Lecithin}]$). The W_0 value of 7.5 was used if not stated otherwise. Upon mixing 0.1 ml of APTMACl solution in water (containing the desired amount of crosslinker) with 15 ml of 0.1 M lecithin solution in cyclohexane, a yellowish transparent gel was formed by vortex mixing. This gel was UV irradiated for 8 h in optically clear glassware. To remove the surfactant, the irradiated organogels were washed several times with a 1:1 (v/v) mixture of acetone and ethyl alcohol. This solvent mixture was chosen because acetone is a precipitant for the hydrogel particles and ethanol is a good solvent for the surfactant.

For nano-sized APTMACl hydrogels, AOT micro-emulsion in isooctane was used, employing the redox polymerization technique at ambient temperature. The polymerization was carried out in $W_0 = 10$ ($W_0 = [\text{H}_2\text{O}]/[\text{AOT}]$) medium with the desired amounts of X ratios. The synthesis of nanogels was accomplished by modifying the previously reported procedure.^{19,20} In a typical route, 0.1 ml of APTMACl was mixed with the crosslinker solution, which was previously prepared with varying amounts of X (0.5-5.0 mol%) in the presence of the accelerator, and 10 μ l of TEMED, and then transferred to a container with 15 ml of 0.1 M AOT solution in isooctane. This solution was vortex stirred to obtain a clear water-in-oil micro-emulsion, which was purged with nitrogen to remove the dissolved oxygen. With the addition of the initiator solution, 1% (with respect to monomer amount) and another 5 μ l of TEMED, simultaneous polymerization and crosslinking reactions were carried out for 24 h by continuously stirring at ambient temperature. The nanogel was then precipitated using excess acetone to destabilize the micelles. Repeated centrifugation and washing with acetone virtually removed all surfactant. The use of AAm as a co-monomer (1:1 mole ratio with respect to APTMACl) also provided copolymeric nanohydrogels that afford rigidity to the network and the ability to control the charge extent in the structure.

Semi-IPN Synthesis and Dye Absorption Studies

The semi-IPNs of the APTMACl micro- and nanogels were prepared by polymerization and simultaneous crosslinking of AAm (a neutral monomer) in the presence of micro- and nanogels. Briefly, various weight

ratios of dried APTMACl microgels (0.5%-5.0% by weight) were mixed with 1 g of AAm containing 0.5 mole% of X (based on AAm) and 2.5 μ l TEMED in 1 ml of distilled water. After meticulously mixing, 0.25 ml of 1% APS (by mole based on AAm) solution was added to this mixture and cast between 2 sealed glass slides. The polymerization and crosslinking reactions proceeded over night. The micro- or nanogel-containing network (semi-IPN) was washed for 5 days with distilled water, daily replacing the water in a shaker to remove any residue from monomer/crosslinker and unbound or unattached microgels.

For dye absorption studies, dried, cleaned, and weighed bulk APTMACl hydrogels were placed in dye solutions (2 drops per 100 ml for food dyes and 1.538E-6 g/ml for FSS) in a constant temperature water bath at 25 °C for 2 days. The microgel-containing semi-IPN was also immersed in similar dye solutions for 2 days. After removing the dye-loaded semi-IPN, they were washed exhaustively for 1 week, changing the wash water twice daily to remove unbound dyes.

Arsenic Absorption

Arsenic absorption experiments were performed in polycarbonate flasks as triplets, using a magnetic stirring setup. To each flask containing 500 ml of 55 ppm As(V) solution was placed 0.2 g of APTMACl dry powdery microgel. Then, 10 ml of As(V) solution was occasionally removed from the absorption media with a syringe attached to a filter (0.2 μ m) to prevent removal of microgel, and the concentration of arsenic was analyzed by an inductively coupled plasma (ICP) optical emission spectrometer (Optima model 5300 DV, PerkinElmer). The dilution effect was taken into account when calculating cumulative arsenic removal.

Hydrogel Particle Characterization

The sizes of the micro- and nanoparticles were investigated by scanning electron microscopy (SEM) (Hitachi High Tech S3000 N) and transmission electron microscopy (TEM) (JEOL JEM 2010 Electron microscope). SEM images were obtained with the water-swollen hydrogel particles on an aluminum SEM stub after lyophilizing. SEM images were acquired at ambient temperature with gold sputtering 2-3 nm thick and an operating voltage of 10-15 kV. For TEM imaging, a drop of nanohydrogel suspension from the AOT emulsion was diluted 60-80 fold with isoctane and placed on a formwar coated copper TEM grid, and dried over night in a closed environment. The TEM images were acquired in vacuum with an operating voltage of 200 keV. For optical microscopy imaging, an Olympus IMT-2 inverted microscope equipped with a high-performance CCD camera (Cohu, Inc., California) and a Leica DM IRE2 inverted microscope equipped with a fluorescent illuminator and a Leica DC350F camera (Leica Microsystems Imaging Solutions Ltd., United Kingdom) were used to image the food dye and fluorescent hydrogel micro-particles. Images were captured using the Image-Pro Plus image analysis system v.5.0 for Windows 2000 and XP (Media Cybernetics, Inc.).

Results and Discussion

With the ability of carrying charges on their backbone, 3-D polymeric networks are very useful materials for biological and environmental applications. For example, negatively charged polymers are generally used for the removal of oppositely charged metal ions and dyes for environmental applications. Positively charged polymers, on the other hand, are generally used in biological applications, i.e. they can neutralize the negative charges of DNA and can be used for delivery purposes in gene therapy, and separation, purification, and/or

pre-concentration of rare species. Positively charged polymer networks can also be used for environmental applications. As shown in Figure 1a, every monomer unit carries its charge to the polymer backbone, making the network polyelectrolyte in aqueous environments. Polyelectrolytes are water soluble and their solubility depends on the ionic strength and the pH of the medium. 3-D networks of polyelectrolytes are charged hydrogels and they swell extensively in the presence of water due to electrostatic repulsion of the charges, and their degree of swelling is highly dependent on the pH and ionic strength of the medium. The swelling behavior and pH response of APTMACl hydrogels were reported in an earlier investigation.¹⁹ Figure 1b shows the digital photo images of shrunken and water swollen APTMACl cationic hydrogels. As can be seen, these hydrogels imbibe enormous amounts of water per gram of dry weight, depending upon their crosslinking ratios.

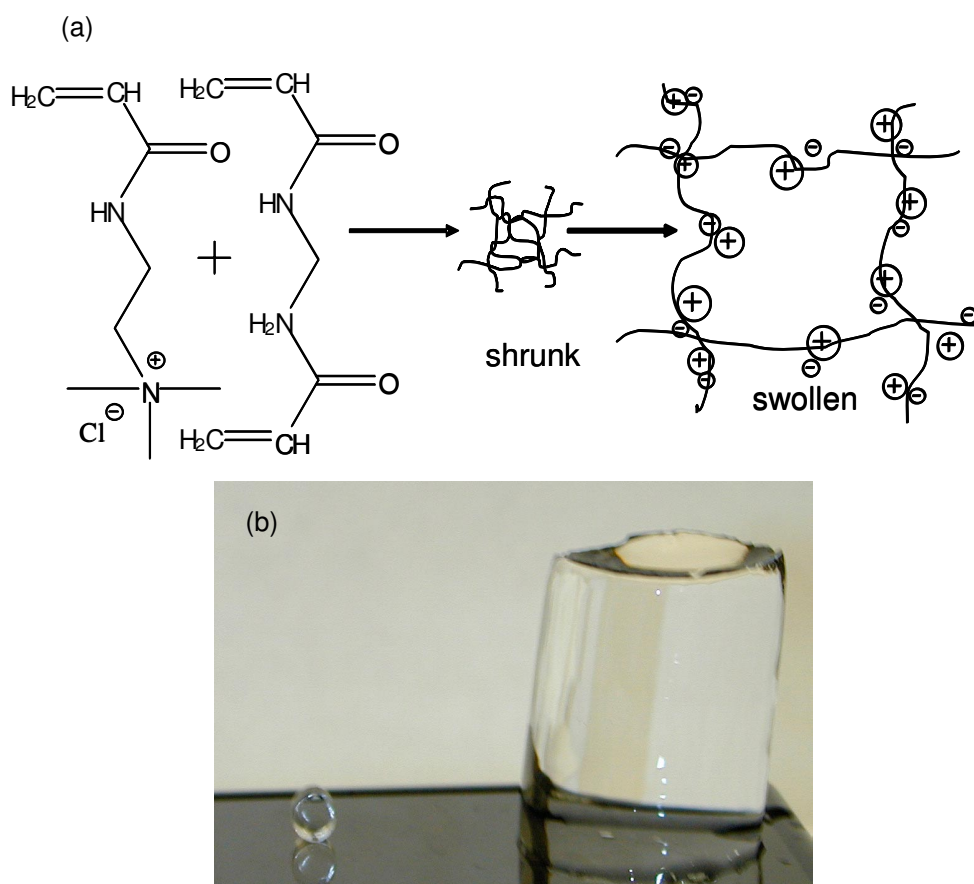


Figure 1. (a) 3-D network formation mechanism from a cationic monomer. (b) Digital photo images of shrunken and water-swollen APTMACl cationic hydrogels.

Given that these APTMACl cationic hydrogels are positively charged, they can be used for the absorption of oppositely charged species, such as dyes. To demonstrate how effectively these cationic structures can be used, solutions of commercially available food dyes, such as FD&C Blue 1, FD&C Red 3, and FD&C Yellow 5, were prepared and contacted with bulk hydrogels. After 2 days of absorption, as described in the experimental section, the cationic hydrogels completely remove the dyes from aqueous environment as depicted in Figure 2a (only red and blue dye solutions are shown). Fluorescence dye is also

negatively charged and can be used for staining or tagging positively charged species. Figure 2b shows the corresponding digital photo images before and after absorption of FFS dye by the cationic hydrogels. Again, it took cationic bulk gels approximately 2 days to completely remove all FFS dye.

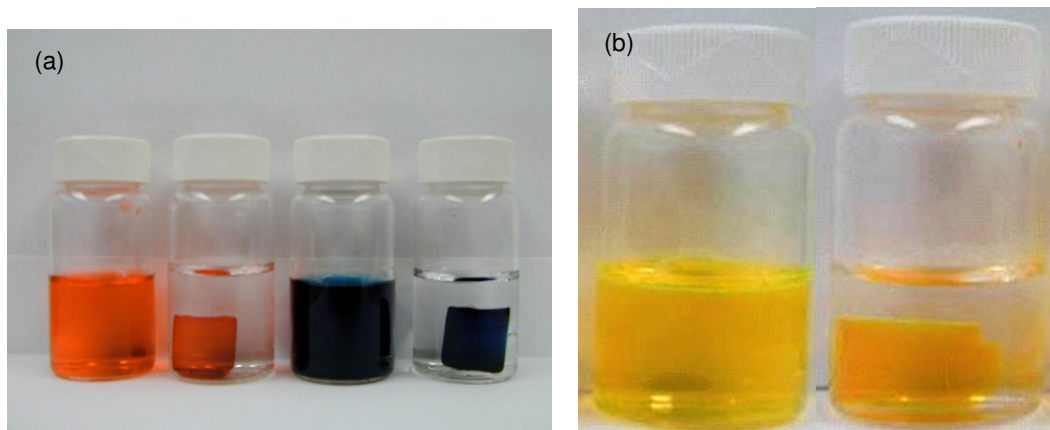


Figure 2. Digital photo images of (a) food dyes and (b) fluorescent dye removal by cationic APTMACl bulk hydrogels.

Although hydrogels are versatile and have many uses, their response time is very long, varying from hours to days. To reduce their response times, they can be synthesized in smaller sizes, such as micro and nano, which expands their areas of application. For this goal, micro-sized APTMACl hydrogels were prepared with a lecithin micro-emulsion system and UV-irradiation of the corresponding organogel (hydrogel precursors and lecithin micro-emulsion). After removing and cleaning the micron-sized cationic hydrogels, water-swollen hydrogels were placed on SEM stubs and freeze dried. As shown in Figure 3, 1% X APTMACl hydrogel has a very broad size distribution, ranging from a few hundred micrometers to sub micrometer size. The cracks seen on the surface of the particles are probably due to the lyophilizing effect. These micron-sized hydrogels reach the maximum degree of equilibrium swelling in 2-3 s in comparison to about 5 h for bulk hydrogels.^{18,19}

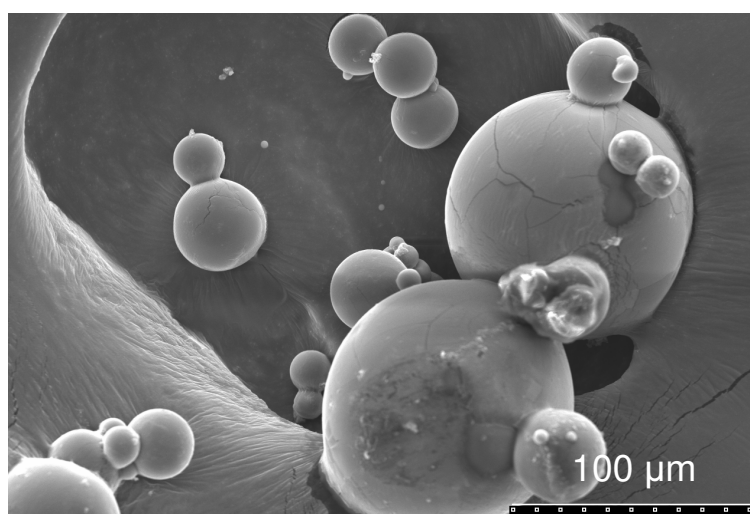


Figure 3. SEM images of freeze dried 1% X APTMACl cationic hydrogel.

To clearly visualize the charge effect and prove the usefulness of cationic micro- and nanohydrogels, an interpenetrating hydrogel-micro/nanogel network (semi-IPN) was prepared as shown in the scheme of Figure 4a. Cationic microgels were mixed with the desired concentration of 5 wt% of a matrix material such as Acrylamide (AAM), which is neutral and contains both a crosslinker and an accelerator (TEMED). After 12-h simultaneous polymerization and crosslinking reactions by the addition of initiator inside sealed glass slides, the obtained semi-IPN network was exhaustively washed, as described earlier, to remove any unbound species, such as microgel, initiator, crosslinker/monomer, and the accelerator. The optical microscopy images of the water-swollen microgel-hydrogel interpenetrating network are shown in Figure 4b. For the matrix material (AAM), 0.5% X (by mole with respect to AAM) was used, while 2 or more mole % crosslinker was used for the cationic micro- and nanogel-synthesized water-in-oil micro-emulsion systems. As AAm is a neutral monomer, the degree of swelling would be less than its charged analogous when an equal amount of crosslinker is used.

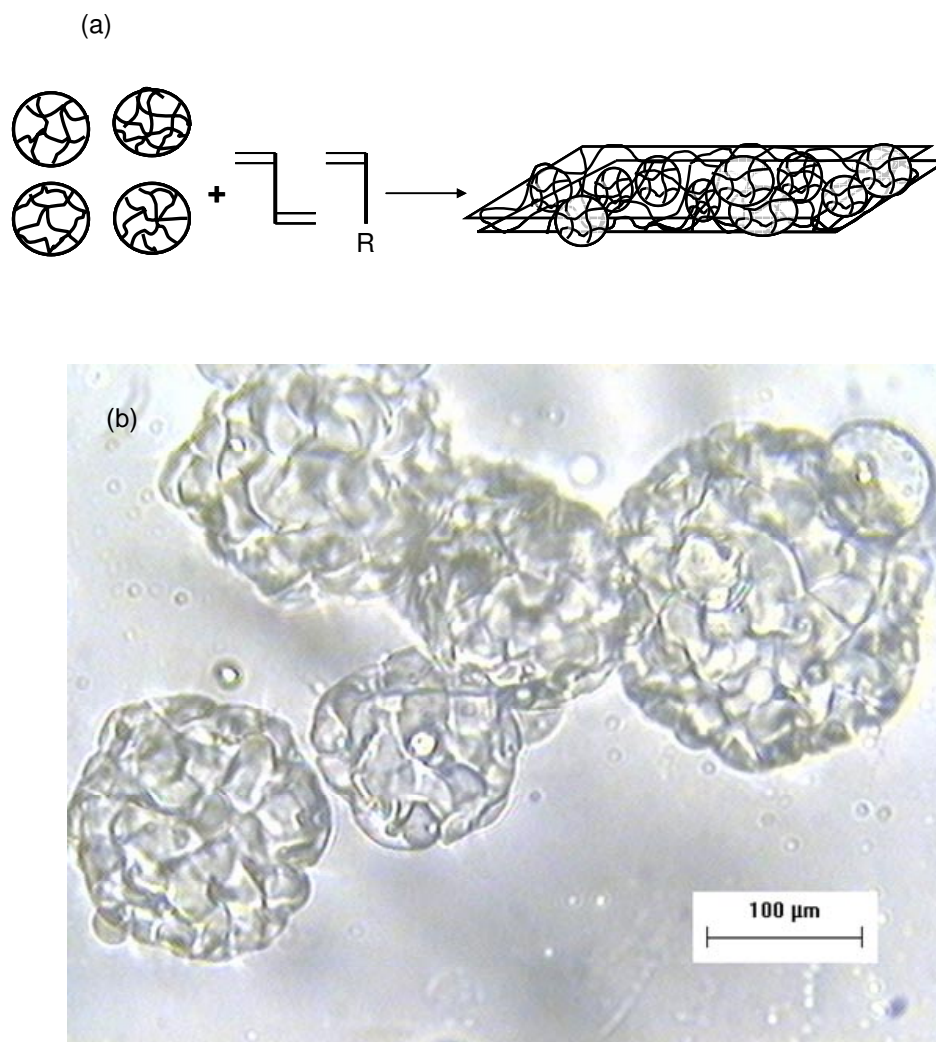


Figure 4. (a) The scheme for interpenetrating the microgel-hydrogel network (semi-IPN) from microgel, crosslinker, and monomer. (b) TOptical microscopy images of water-swollen cationic microgel embedded in the neutral AAM matrix (semi-IPN) (microgel is 1% X and AAM is 0.5% X).

The optical microscopy images of red and blue food dye absorbed by the microgel-hydrogel semi-IPN, respectively, are shown in Figure 5a,b respectively. The most striking feature of this image is the color of the microgels. The matrix material, AAm, is neutral and the dye molecules are negatively charged; only positively charged microgels can be responsible for the dye absorption as seen in the image. This characteristic is more pronounced and can be clearly visualized when fluorescent dye is used. As illustrated in Figure 5c, the fluorescent color (bright yellow-green) comes only from the FFS dye, which is absorbed by the microgels, not the AAm matrix. The dark background in the image is the AAm matrix, which has no dye. It is also noteworthy to mention that after the absorption studies with food dyes and FFS dye, the microgel-hydrogel IPNs were washed with water, for 5 d, replacing the water twice daily. When complete, the staining can only be visually discerned in/on the microgels, not in the AAm matrix.

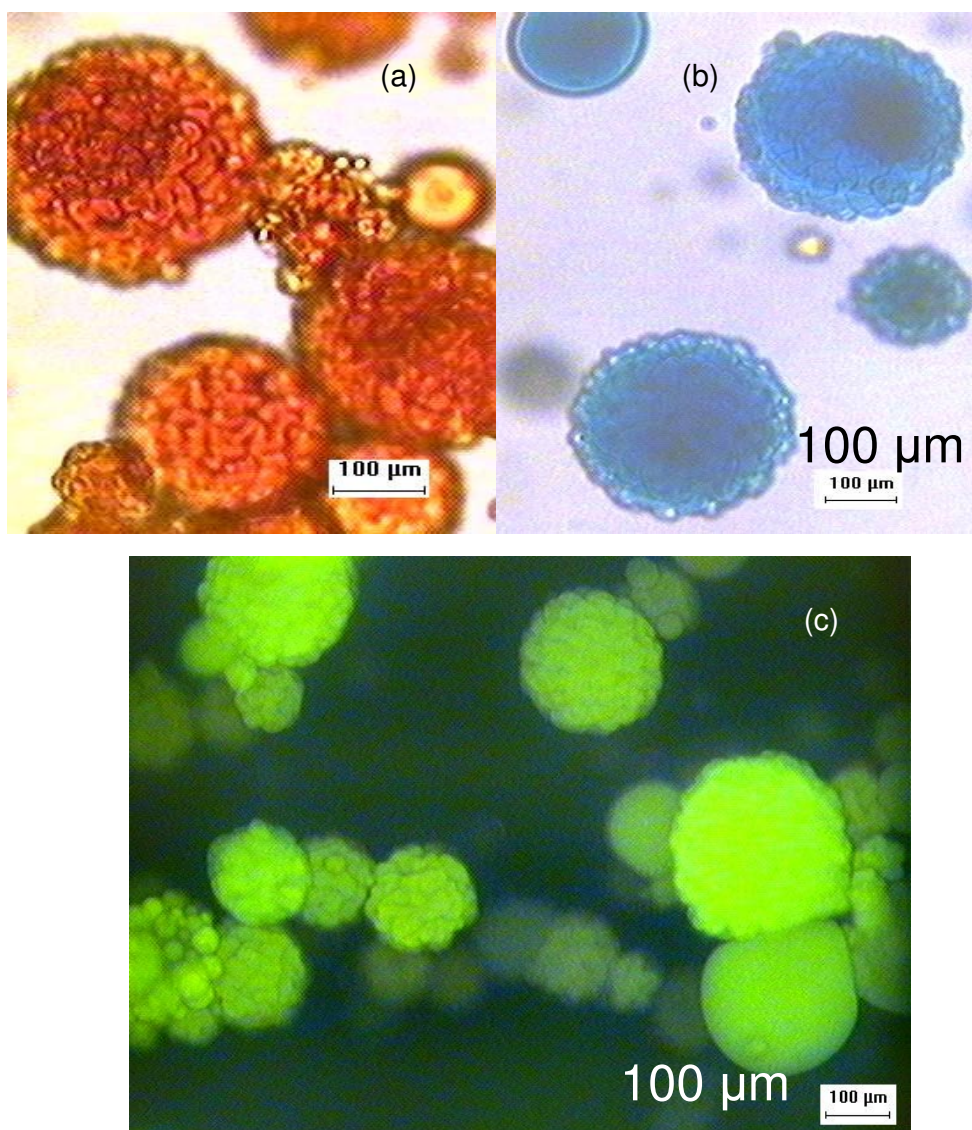


Figure 5. Optical microscopy images of red and blue food dye absorbed into the microgel-hydrogel network (a and b). (c) Fluorescence microscopy images of the microgel-hydrogel IPN (microgel is 1% X and the matrix (AAm) is 0.5% X).

The other possible use for the hydrogels is the removal of arsenic, which is one of the most important species that contaminate drinking water and a longstanding environmental issue. To date, various adsorbents have been used for the removal of arsenic from an aqueous environment, such as inorganic clays, zeolites, titanium dioxides, ion exchange resins, etc.^{15,16,17,18} However, to the best of my knowledge, there are no reports of micro- or nanohydrogel being used for the removal of arsenic. It was shown here for the first time that these microgels can effectively be used for the removal of As(V) from an aqueous environment. Although arsenic has various oxidation states, depending on the pH of the medium, As⁵⁺ is the most common form and usually dissolves as [AsO₄]³⁻ in its aqueous solutions.^{15,16,21} Figure 6 shows the removal of As(V) from an aqueous environment by a cationic APTMACl microgel. As shown in Figure 6, the removal efficiency was very high, as the concentration of As(V) dropped from 55 to 3.9 ppm in less than 10 min (9.6 min) after contacting with the APTMACl microgel. Afterwards, there was no significant change in the concentration of As(V) (for up to 2 h of absorption), indicating that ~96% of the As(V) was removed by 0.2 g of APTMACl microgel in about 10 min from 500 ml of 55 ppm As(V) solution.

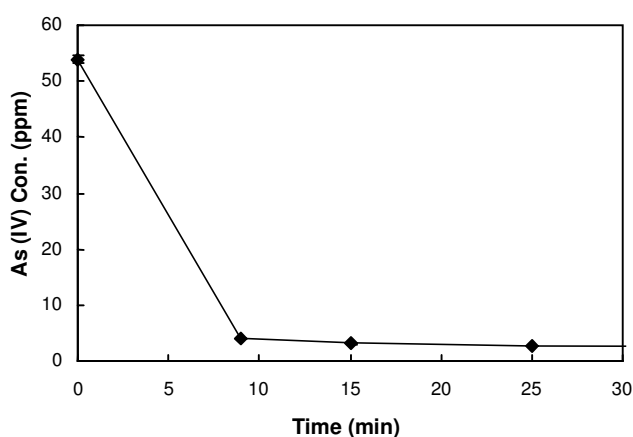


Figure 6. Arsenic removal from an aqueous environment by cationic APTMACl cationic microgels.

Additionally, nano-sized cationic hydrogels can also be prepared with a micro-emulsion system. To prepare cationic nanogels, AOT was used as a surfactant and the TEM image of the resultant nanogels are shown in Figure 7a,b. Figure 7a is the TEM image of the 1% crosslinked cationic APTMACl nanohydrogel, while 7b is the copolymer of APTMACl with AAm in a 50:50 mole ratio. The use of AAm provides rigidity to the structure and the ability to tune the charges in the nanonetwork. The digital photo images shown in Figure 7c are the AAm matrix (1), microgel-hydrogel semi-IPN (2), and FFS dye absorbed by microgel-hydrogel semi-IPN (3), nanogel-hydrogel semi-IPN (4), and nanogel-hydrogel semi-IPN (5), respectively. The nanogel-containing semi-IPN was prepared as described in Figure 4a, except that microgels were replaced with nanogels. Fluorescence microscopy images of (5) are not shown because there was no discernable particle in the network; the matrix was completely yellow-green, indicating the complete distribution of nanogels in the network. This is reasonable due to the small size of nanogels (~5 nm in dry state) and the resolution of fluorescence microscopy, which is in the order of few micrometers. These images are shown to justify the fact that nanogels can also be used as adsorbent for the removal of environmentally harmful materials, such as dyes and toxic metal ions. It was demonstrated (Figure 6.) that the microgels removed 96% of arsenic in about 10 min; hence, it is plausible to assume that nanogels might do the same to an order of seconds. To overcome some drawbacks, such as how these nanogels can be handled, nanogels could

be embedded into a secondary matrix as shown in Figure 7(c) (4 and 5), which can be used for practical applications. As arsenic is labile and can have various oxidation states, so can hydrogels, and hydrogels can be engineered to have various charges and sizes with different architectures, as shown in this investigation. In fact, the current investigation demonstrated the use of such materials for the removal of environmentally hazardous materials, including arsenic and its various complexes.

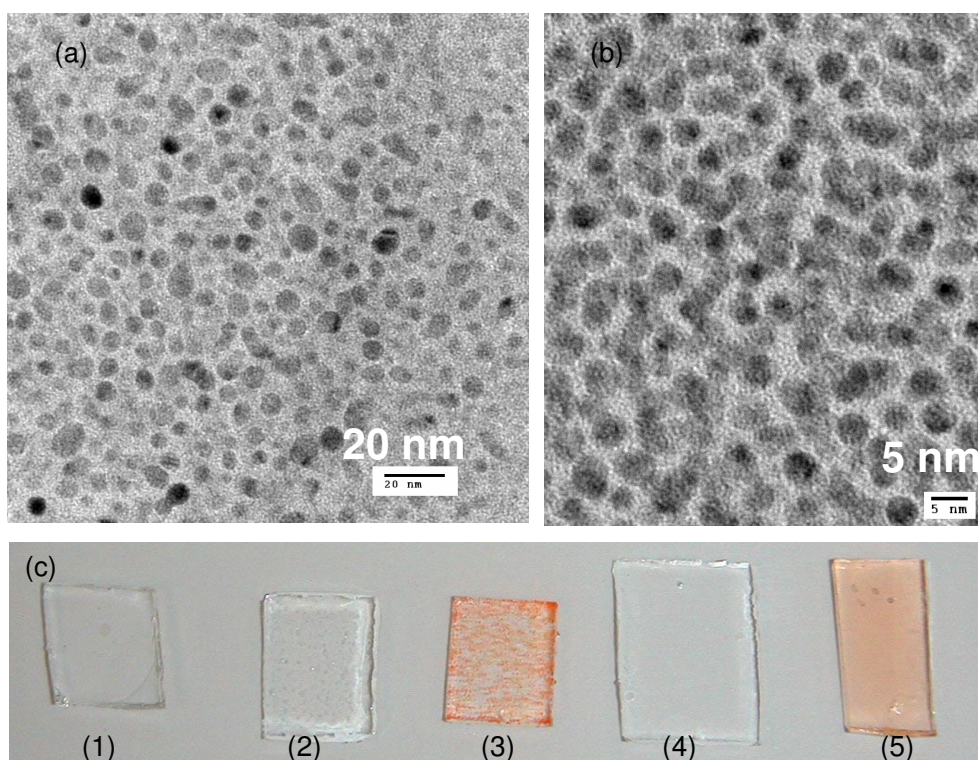


Figure 7. TEM images of 1% crosslinked cationic APTMACl nanohydrogel (a) and copolymer of APTMACl with AAm in 50:50 mole ratios (b). Digital photo images (c) of the AAm matrix (1), microgel-hydrogel IPN (2), and FFS dye absorbed by microgel-hydrogel IPN (3), nanogel-hydrogel (IPN) (4), and FFS absorbed nanogel-hydrogel IPN (5), respectively.

Conclusion

This investigation showed that cationic hydrogel can be prepared in variety of sizes (bulk, micro-, and nano-sized). The hydrogels prepared in this study were proven to be very useful for environmental applications, such as the removal of dyes and toxic metals from an aqueous media. Moreover, their tunable sizes and variety of architectural designs, such as micro, nano, and hydrogel-hydrogel semi-IPN, their types of charges, and the degree that these variables can be controlled by the appropriate choice of co-monomers were shown. In fact, having both cationic and anionic charges on the micro- or nanogel provides additional advantages for the removal of 2 distinct species simultaneously. Hydrogels are versatile and viable materials with many potential potentials for environmental applications.

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