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PAPER

## Nanoparticle-crosslinked hydrogels as a class of efficient materials for separation and ion exchange†

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We describe the remarkable capabilities of polymer–nanoparticle hybrids for cation binding and separation. The materials investigated here are hydrogels of *N*-isopropylacrylamide (NIPA) prepared using nanoparticles of the synthetic clay, Laponite® RD, as the crosslinkers. When immersed into an aqueous solution containing a cationic amine-based dye (methylene blue), the gel rapidly soaks up the dye from solution. Additionally, the gel is able to selectively extract the above cationic dye from a mixture of cationic and anionic dyes. These ion-exchange properties are driven by the strong binding affinity of certain cations for the anionic surfaces of the clay nanoparticles within the gel matrix. A comparison of the nanostructured gel with a typical cation-exchange resin (polystyrene-sulfonate) shows that the former is quicker and more efficient at extracting cationic species from solution. We also show that the solute adsorbed within the gel can be further concentrated by exploiting the shrinking property of NIPA gels when heated. Additionally, we demonstrate the disassembly of Laponite-crosslinked gels by exposure to an organic solvent or a hydrophilic oligomer, which allows the adsorbed solute to be released and thereby recovered.

### Introduction

Hydrogels are three-dimensional polymer scaffolds swollen in aqueous liquid.<sup>1,2</sup> In particular, hydrogels of acrylamide (AA) and its derivatives such as *N*-isopropylacrylamide (NIPA) have become workhorses for polymer research since the 1980s.<sup>1–4</sup> These gels are known for their temperature-dependent response—in particular, NIPA hydrogels shrink when heated above their lower critical solution temperature (LCST), which is around 34 °C.<sup>3,4</sup> Typically, NIPA gels are made by polymerizing the NIPA monomer with a multifunctional moiety such as *N,N'*-methylene bis-acrylamide (BIS). However, as shown by Haraguchi and co-workers,<sup>5–7</sup> it is also possible to make NIPA gels using clay nanoparticles rather than BIS as the crosslinkers (Fig. 1a). A few different types of clay particles can be used for this purpose, many of which are synthetic layered silicates from the Laponite® family. Clay-crosslinked gels have been shown to have a range of remarkable properties, including high pore

volumes, large swelling ratios, and high mechanical strength and extensibility.<sup>5–9</sup>

Nanoparticles of clays such as the Laponites are known to have numerous negative charges on their surface, which are nominally bound to sodium counterions.<sup>10</sup> In aqueous dispersion, the sodium ions can be exchanged for other cations, especially those based on tertiary or quaternary amines.<sup>11,12</sup> Despite their binding affinity for cations, the direct use of clays as ion-exchange materials in water has its disadvantages. Specifically, pH and ionic strength affect the stability and dispersibility of clay particles.<sup>10,13</sup> Moreover, clay particles can flocculate and form gels in water—if so, it is not easy to separate cation-bound clay particles from the rest of the sample.<sup>10,13</sup> Thus, clays are not the current materials of choice for cation-exchange; rather it is crosslinked resins of strongly anionic polymers such as polystyrene-sulfonate (PSS).<sup>14</sup> Such resins are commercially available (e.g., Rexyn® beads) and find use as stationary phases for chromatographic separations as well as for waste-water remediation.

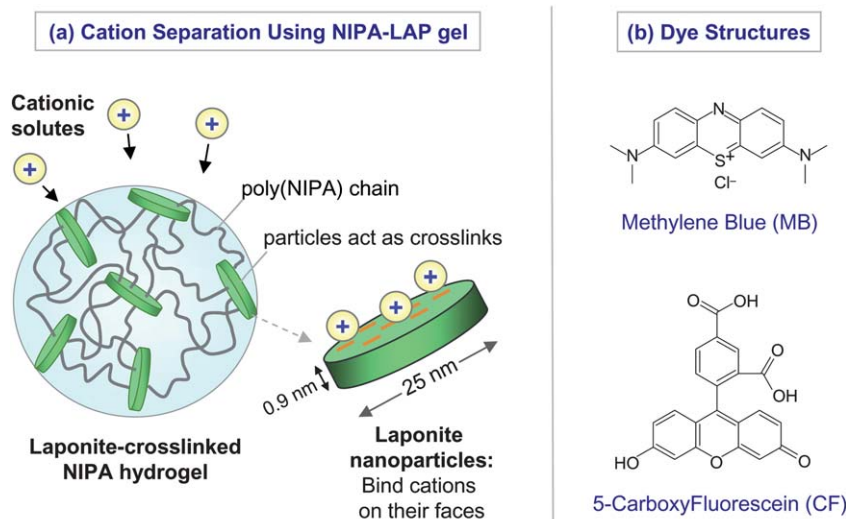
In this paper, we describe the use of clay-crosslinked NIPA gels for cation-binding and separation. The clay used here is Laponite® RD, a synthetic layered silicate clay that is in the form of disk-like nanoparticles with a diameter of 25 nm and a thickness of 0.9 nm (Fig. 1a). The presence of these nanoparticles within the gel affords a substantial surface area for binding of amine-based cations and thereby transforms ordinary hydrogels of NIPA into efficient separation materials.<sup>15–18</sup> Moreover, because the clay particles are crosslinks or nodes in the gel

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**Fig. 1** (a) Schematic of a laponite-crosslinked NIPA hydrogel. The laponite particles are disks with a diameter of 25 nm and a thickness of 0.9 nm. When polymerized with NIPA and initiator, the particles form bonds with several NIPA chains and thereby the particles serve as the crosslinks in the gel network. The particles also have numerous negative charges on their faces, which present binding sites for cations. Cationic solutes can thus diffuse into the gel and get adsorbed on the particles. (b) Structures of the cationic dye (MB) and anionic dye (CF) used in this study.

network, they are insensitive to the pH or ionic strength of the solution. Thus, clay-bearing gels are shown to be useful for separations over a much wider range of conditions than the clay particles by themselves. Also, clay-crosslinked gels are demonstrated to outperform conventional PSS-based ion-exchange resins in their ability to extract a cationic dye from aqueous solution.

Our study also exploits the unique nature of the polymer matrix in the above gels. Specifically, NIPA-clay gels exhibit the same thermosensitive swelling and shrinking behavior as NIPA-BIS gels, and this property is used to concentrate the bound solutes after adsorption. Also, NIPA-laponite gels are shown to have a feature that is distinct from conventional gels, in that these gels can be *disassembled* (liquefied) by exposure to certain organic solvents such as dimethylformamide (DMF) or oligomeric polyethylene glycol (PEG). To our knowledge, this is the first report of solvent-induced disassembly in such gels, and this has profound implications regarding the nature of the bonds between the polymer chains and the clay nanoparticles. We show that this capability for gel disassembly is useful in the context of separations in offering a strategy for recovering the bound solute.

## Experimental section

### Materials

The monomers *N*-isopropylacrylamide (NIPA), sodium acrylate (SA), and *N,N'*-methylene-bis(acrylamide) (BIS); the initiator potassium persulfate (KPS); and the catalyst *N,N,N',N'*-tetramethylethylenediamine (TEMED) were all purchased from Sigma Aldrich. Laponite® RD and Laponite® XLG were obtained from Southern Clay Products. Rexyn I-300 (H–OH) beads were purchased from Fisher Scientific. The dyes, methylene blue (MB, cationic) and 5-carboxyfluorescein (CF, anionic), were purchased from Sigma Aldrich. The structures of these dyes are shown in Fig. 1b.

### Hydrogel preparation

Two types of hydrogels were prepared for this study: clay cross-linked and BIS crosslinked. Clay crosslinked gels (henceforth denoted as NIPA–LAP) were prepared by first dispersing laponite RD (0.2–0.4 g) in 10 mL of nitrogenated deionized water using a vortex mixer. NIPA monomer (1 g), KPS initiator (0.01 g) and TEMED catalyst (24  $\mu$ L) were subsequently added to the dispersion. This pre-gel solution was then filtered through a membrane with a 0.45  $\mu$ m pore size. The filtered pre-gel solution was poured into 4 mL glass vials and polymerized at room temperature over a period of 6 h. The final gel was a cylinder of  $\sim$ 1 cm diameter and 3 cm height. NIPA–SA–BIS gels were prepared by combining NIPA (0.7 g), SA (0.3 g), BIS (0.0133 g), KPS (0.01 g), and TEMED (24  $\mu$ L) with 10 mL of nitrogen-purged water, followed by polymerization as above. After polymerization was complete, the bulk gels were washed with deionized water for 24 h prior to use. To prepare gel flakes, bulk gels were first dehydrated by placing in a vacuum oven overnight at room temperature. These dehydrated gels were then crushed into flakes of  $\sim$ 5 mm size and used as is.

### Solute separation experiments

MB and CF were used as model cationic and anionic solutes. A given gel (either flakes or cylinder) was placed in a solution of the dye(s) in distilled-deionized (DI) water (50 mL) without stirring. UV-Vis spectrometry (Cary 50 spectrometer) was used to quantify dye removal from solution over a period of 72 h. Comparative studies of dried gel flakes and Rexyn beads were performed by adding specific weights of the materials into separate 50 mL solutions of the dye(s). For adsorption isotherm studies, cylindrical gels (NIPA–LAP or NIPA–SA–BIS) were placed in 50 mL of solutions containing varying concentrations of MB. The gels were allowed to adsorb MB until equilibrium

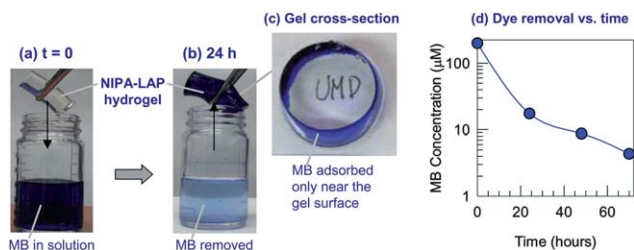
was reached; equilibrium was determined when the concentration of MB in the surrounding solution no longer changed.

## Results and discussion

### Separation of the cationic dye from aqueous solution

Laponite RD nanoparticles, due to their anionic surfaces, have the ability to adsorb cationic solutes from solution. In a NIPA-LAP gel, these particles form the crosslink points or junctions, and are thereby fixed in place (Fig. 1a).<sup>5-7</sup> While the particles cannot leave the gel, water and small solute molecules can freely diffuse into the gel. Thus, cationic solutes, especially those based on tertiary or quaternary amines,<sup>11,12</sup> can adsorb on the surfaces of the particles. Moreover, because the particles within the gel are immobilized, they are not susceptible to colloidal interaction forces, and hence do not undergo flocculation or precipitation regardless of the pH or ionic strength of the surrounding environment. NIPA-LAP gels can thus offer superior separation properties over the bare laponite particles.

Separation of the cationic tertiary-amine-based dye, MB, from aqueous solution by a NIPA-LAP gel was initially studied as follows. First, a solution in DI water of 200  $\mu\text{M}$  MB was prepared. Then, 50 mL of this solution was taken in a container and a cylindrical gel (1 cm diameter, 3 cm tall) of NIPA-LAP was immersed in it. The laponite and NIPA concentrations in this bulk gel were 30  $\text{mg mL}^{-1}$  and 100  $\text{mg mL}^{-1}$ , respectively. Note from the photograph in Fig. 2a that the gel is initially clear while the solution has a deep blue color from the dye. The concentration of MB in solution as a function of time is plotted in Fig. 2d. The data reveal that 90% of the dye in the solution is removed by the gel within 24 h, and about 98% of the dye is removed by 72 h. Photographs of the gel and solution after 24 h are shown in Fig. 2b—note that the gel has a deep blue color while the solution is a faint blue. When this gel is sectioned (Fig. 2c), a distinct layer of adsorbed dye can be seen near the surface of the gel while the center is observed to be clear of the dye. This shows a strong affinity of MB cations for the surfaces of laponite RD particles; such strong binding affinity ensures that the cations get adsorbed well before they can reach the center of the gel.

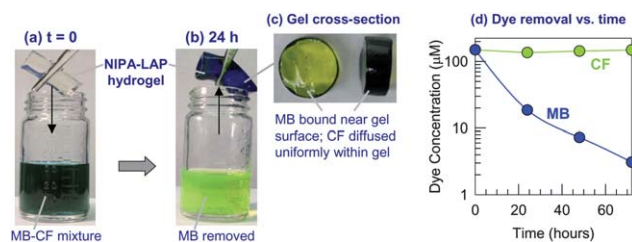


**Fig. 2** Separation of a cationic dye, methylene blue (MB), from the solution by a laponite-crosslinked NIPA gel. (a) At time zero, the cylindrical gel is immersed into the MB solution. (b) Within 24 h, the gel has removed most of the MB from the solution. Note that the solution has a much lighter blue color compared to its original state. On the other hand, the gel takes on a deep blue color due to the dye. (c) Cross-section of the gel shows that the dye is confined to a thin layer near the surface whereas the core is colorless and transparent. (d) Plot of dye concentration vs. time.

We then compared the separation properties of NIPA-LAP gels with those of a conventional ionic hydrogel. The latter was prepared by copolymerizing NIPA (70  $\text{mg mL}^{-1}$ ) with an anionic monomer, SA (30  $\text{mg mL}^{-1}$ ), and using BIS as the crosslinker. The overall polymer concentrations are identical between the NIPA-LAP and the NIPA-SA-BIS gels, but the latter is expected to have 25 times as many anionic groups compared to the former. Despite the stronger anionic character, however, the NIPA-SA-BIS gel was much less efficient at removing MB cations from solution compared to the NIPA-LAP gel. The differences between the two gels are depicted in adsorption isotherms (ESI†, Fig. S1). Data for both gels can be fitted to the Langmuir adsorption isotherm, and the results show a much higher binding affinity (adsorption constant) of MB for the NIPA-LAP gels. Also, when a NIPA-SA-BIS gel is sectioned, the blue color from MB is observed throughout the gel (ESI†, Fig. S1). This indicates that some of the weakly binding MB is able to diffuse into the interior of the NIPA-SA-BIS gel before it is adsorbed. In contrast, the strong affinity of MB for laponite particles causes it to be localized near the NIPA-LAP gel surface (Fig. 2c).

We have studied MB separation using NIPA-LAP gels in buffers at various pH values (4, 7, and 10). The results (ESI†, Fig. S2) were nearly identical for these three cases, indicating that the adsorption of MB onto laponite particles was unaffected by pH. Note that an aqueous dispersion of laponite RD particles typically becomes destabilized at pH below 9.<sup>10,13</sup> These results confirm that when the particles are part of the gel network, they are protected against flocculation. NIPA-LAP gels can thus function as separation media over a wide range of pH.

Next, we investigated the use of NIPA-LAP gels to separate the cationic MB from a mixture containing MB along with the anionic dye, CF. Both dyes at initial concentrations of 150  $\mu\text{M}$  were mixed into DI water, and as before, a cylindrical gel of NIPA-LAP (laponite and NIPA concentrations of 30 and 100  $\text{mg mL}^{-1}$ , respectively) was immersed in 50 mL of the mixture (Fig. 3a). Initially, the solution has a blue-green color reflecting the simultaneous presence of both dyes. Fig. 3d shows the dye concentrations in solution as a function of time. Again,



**Fig. 3** Separation of a cationic dye from a mixture of cationic and anionic dyes. (a) At time zero, the laponite-crosslinked NIPA gel is immersed into a mixture of MB (cationic) and CF (anionic) dyes. (b) Within 24 h, the gel has removed most of the MB from the solution. The solution thus has the yellow-green color due to CF, while the gel is colored blue due to the MB. (c) Cross-section of the gel shows that the MB is confined to a thin layer near the gel surface whereas the CF is diffused uniformly within the gel core. (d) Plot of dye concentration vs. time confirms a sharp drop in MB concentration while the CF content remains nearly constant.

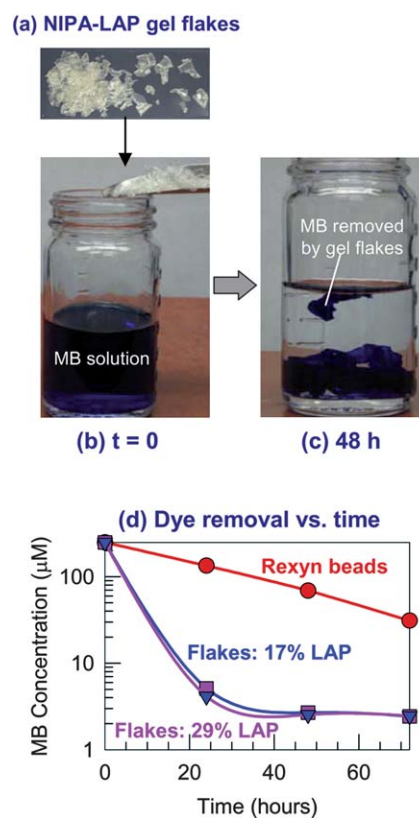
about 98% of the cationic MB is removed by the gel within a period of 72 h. In contrast, the concentration of CF decreases only slightly over this time period. Photographs of the solution and gel after 24 h are shown in Fig. 3b—at this point, about 90% of the MB has been removed by the gel. Accordingly, the gel has a deep blue color due to the MB while the solution has the yellow color characteristic of CF. In this case also, the gel was subsequently sectioned and examined. Again, as shown by Fig. 3c, a distinct dark blue layer of adsorbed MB can be observed near the gel surface. In comparison, a yellow color due to the anionic CF is uniformly distributed throughout the gel. Incidentally, when this gel was then placed in water, the CF eventually diffused out of the gel leaving the center colorless again while the layer of MB remained (data not shown). These observations reflect the strong binding of the cationic MB to the particles, and the lack of binding of the anionic CF. In sum, the NIPA–LAP gel is effective at selectively removing MB from the mixture of dyes.

### Comparison with other cation-exchange media

It is useful to compare NIPA–LAP with other materials used for cation exchange. In this context, we note from the above photographs of gel cross-sections that a macroscopic gel of NIPA–LAP is an inefficient use of the material because the dye is adsorbed only on the laponite particles present within a thin layer close to the gel surface. By decreasing the gel size, the surface area for adsorption can be substantially increased, thereby enhancing the efficiency of separation. Accordingly, we dehydrated a NIPA–LAP gel and crushed this dehydrated material into irregular flakes. As shown by the photograph in Fig. 4a, the flakes are roughly 1 mm in their smallest dimension and about 5 mm in their longest dimension. The initial bulk gel had laponite and NIPA concentrations of 20 mg mL<sup>-1</sup> and 100 mg mL<sup>-1</sup>, respectively. Assuming complete removal of water, the flakes are composed of laponite and NIPA in a weight ratio of 20 : 100, which translates to 17 wt% of laponite. We then added 0.3 g of these flakes to a solution of 250 μM MB in DI water (50 mL volume), and the mixture was left on the bench without stirring. As expected, the gel flakes were much more efficient at dye removal compared to the bulk gel. The plot of dye concentration vs. time in Fig. 4d shows that about 97% of the dye is removed within 24 h. Additionally, the photograph after 48 h (Fig. 4c) shows blue gel flakes at the bottom of a clear solution that has only a faint tint of blue.

We then compared NIPA–LAP flakes with commercially available beads of Rexyn® ion-exchange resin. These beads are crosslinked polystyrene latex particles (<1 mm in overall diameter) and are stated by the manufacturer to have “medium porosity”. The beads used here comprise both anionic (sulfonate, SO<sub>3</sub><sup>-</sup>) and cationic moieties for ion-exchange.<sup>14</sup> We added 0.6 g of Rexyn beads to an identical 250 μM solution of MB. As shown by Fig. 4c, the beads caused a linear decrease in the concentration of MB; however, significant MB still remained in solution after 72 h. Thus, the NIPA–LAP flakes are seen to be much more efficient at separation of the MB dye compared to the commercial ion-exchange resin.

As stated by the manufacturer, the cation exchange capacity (CEC) of the Rexyn beads is 0.46 mEq g<sup>-1</sup>. In comparison, the laponite particles have a CEC of 0.55 mEq g<sup>-1</sup> and by extension,



**Fig. 4** Cationic dye removal by NIPA–laponite gel flakes vs. Rexyn ion-exchange beads. (a) Gel flakes of ~5 mm in their largest dimension are obtained by dehydrating a bulk NIPA–laponite gel. (b) At time zero, these flakes are added to an MB solution. (c) Within 48 h, the flakes remove almost all the dye—note the clear solution coexisting with the flakes. (d) Plot of dye concentration vs. time for two sets of gel flakes with different laponite contents and for Rexyn beads. The rate of dye removal by the beads is much slower compared to the gel flakes. The laponite content in the gel flakes (blue triangles = 17 wt% vs. pink squares = 29 wt %) does not affect the rate of dye removal.

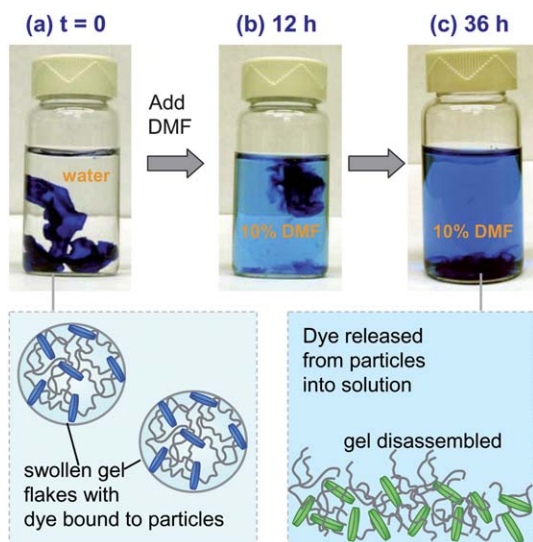
the CEC of NIPA–LAP flakes (for 17 wt% laponite) is only 0.09 mEq g<sup>-1</sup>. Considering their smaller overall size and larger CEC, one would expect the Rexyn beads to be superior at dye separation; however, the results indicate otherwise. A likely reason for the greater efficiency of NIPA–LAP gel flakes is that the flakes have larger pore sizes (due to larger distances between the particulate crosslinks), allowing more facile diffusion of solutes into the gel flakes for adsorption. In this context, it is interesting to compare our results for gel flakes with varying proportions of laponite (29 vs. 17 wt%). These two sets of gel flakes exhibited about the same propensity for separating MB, as shown by Fig. 4c. The results can be explained as follows: while a higher laponite content implies more sites for solute adsorption, it also implies smaller pore sizes for the gels, which hinders solute diffusion. Thus, a low proportion of laponite in the gel flakes is adequate and possibly better for efficient separation.

### Solute recovery and concentration

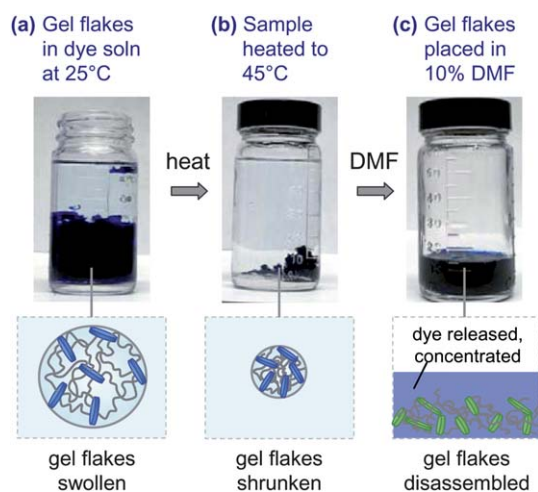
We have found that when a NIPA–LAP gel is placed in an aqueous solution containing dimethylformamide (DMF), tetrahydrofuran (THF) or short-chain polyethylene glycol (PEG), the

gel gets disassembled over time. This property can be put to use in the recovery of bound solute, as illustrated by the following experiment. For this, we collected the NIPA–LAP gel flakes with adsorbed MB, such as those at the bottom of the container in Fig. 4b, and placed these dye-bearing flakes in an aqueous solution containing 10% DMF (Fig. 5a). Over several hours, we observed a reduction in the volume of the gel flakes, and correspondingly, the blue color from the dye began to appear in the solution (Fig. 5b). Evidently, some of the dye is desorbing from the particles and diffusing out of the gel. As time progressed, the blue color intensified in solution, and a precipitate was observed at the bottom of the container (Fig. 5c). Preliminary studies suggest that the precipitate contains most of the poly(NIPA) and laponite, while a large fraction of the dye within the original gel flakes is released into the solution. Thus, the bound cationic dye can be recovered from the gel flakes by exposure to DMF. Similar effects were also observed when the gel flakes were placed in either 10% THF or 10% PEG of molecular weight  $300 \text{ g mol}^{-1}$ .

The above phenomenon of solvent-induced disassembly was also observed with bulk NIPA–LAP gels. When a bulk gel was placed in a solution of 10% DMF, the gel became softer and more floppy within a few hours, indicating a loss of internal crosslinks within the network. Correspondingly, the gel also began to swell more. With time, the swelling and softening continued until one could no longer distinguish the gel from the solution. At this point, the disassembly of the gel was essentially complete—it had been converted from a solid to an amorphous liquid. To our knowledge, such disassembly phenomena have not been reported before for clay-crosslinked gels. In previous studies, the gels have typically been prepared using the procedure put forth by Haraguchi *et al.*,<sup>5–7</sup> which calls upon the use of



**Fig. 5** Recovery of bound solute through gel disassembly. (a) When NIPA–laponite gel flakes with bound MB dye are placed in water, the flakes are swollen but the dye remains in the gel, as shown by the schematic. (b) Addition of DMF to the water causes the gel to disassemble and the MB to be released into the solution. (c) The disassembly and MB release continue with time, as evidenced by the increasing blue color of the solution. Fragments of disassembled gel form a precipitate, which likely contains all the poly(NIPA) and the laponite particles, as indicated by the schematic.



**Fig. 6** Method to concentrate and recover the bound solute. (a) NIPA–laponite gel flakes are added to a large volume of MB dye solution at  $25 \text{ }^\circ\text{C}$ . When dye removal is complete, the blue flakes are swollen. (b) The sample is then heated to  $45 \text{ }^\circ\text{C}$ , which is above the LCST of NIPA. This causes the flakes to shrink considerably, while the dye remains within them. (c) The shrunken flakes are removed and transferred to a small volume of 10% DMF solution. The solvent disassembles the gel and the dye is released into the solution. Overall, the dye concentration is increased 5-fold by this process.

laponite XLG, a clay that is chemically quite different from the laponite RD employed here. To test whether the type of laponite makes a difference, we also prepared NIPA gels with laponite XLG, and those were also found to disassemble upon exposure to DMF.

The mechanism for solvent-induced disassembly of NIPA–LAP gels is not known at this point. However, we believe our findings shed light on the nature of the bonds between laponite particles and the poly(NIPA) chains. According to Haraguchi *et al.*, the polymer chains are fixed to the faces of the laponite particles by bonds that are polar or ionic in character rather than covalent bonds.<sup>19–23</sup> The same laponite faces, with their numerous negative charges (Fig. 1a), are also the sites for adsorption of cationic dye molecules. We speculate that in the presence of DMF, THF, or PEG the binding sites on the laponite particles lose their strong affinity for both the poly(NIPA) chains as well as the dye molecules. As a result, the dye molecules and the polymer chains are both displaced from the particle surfaces. In turn, this implies the elimination of crosslinks from the gel network, and consequently, an increase in the mesh size of the gel. The gel therefore swells greatly and loses its mechanical integrity. The displaced dye molecules can then freely diffuse out of the gel and into the solution. In sum, our results show that solvents can be used to disassemble NIPA–LAP gels “on command”, and this offers a convenient way to recover the bound ionic solute.

Finally, we show how gel disassembly can be combined with the thermo-responsive nature of NIPA gels in an intriguing way. As mentioned in the Introduction, NIPA–BIS gels are known to undergo a volume transition from swollen to shrunken when the temperature is increased above the LCST of the polymer, which is about  $34 \text{ }^\circ\text{C}$ .<sup>3,4</sup> Much like NIPA–BIS gels, NIPA–LAP gels also show the same volume transition above the LCST. We

exploit this property to *concentrate* the solute adsorbed within a NIPA–LAP gel. This is shown in Fig. 6. First, we add NIPA–LAP gel flakes to an MB solution at room temperature (23 °C). The flakes are able to bind and remove the majority of the dye from solution, as has been demonstrated previously in Fig. 4. The photograph in Fig. 6a also shows that the flakes are considerably swollen at this temperature. Next, the temperature is increased to 45 °C (above the LCST). As shown by Fig. 6b, this causes the flakes to shrink considerably. Note that the shrunken flakes still retain the bound MB, *i.e.*, there is no leakage of dye into the external solution at this temperature. We then remove the flakes from the solution by filtration and immerse it in a smaller volume of aqueous solution containing 10% DMF at 45 °C. The solvent induces disassembly of the gel and the ionic solutes are released into the solution (Fig. 6c). Once the precipitate of poly(NIPA) and laponite is filtered away, we are left with a solution of the dye at a *much higher concentration* compared to the original solution. Thus, the solute can not only be separated by the NIPA–LAP gel but it can also be subsequently recovered in a concentrated form. This ability to concentrate and recover the solutes can prove useful for the extraction of dilute, but valuable solutes.

## Conclusions

We have demonstrated that NIPA–LAP gels, where the laponite particles form the crosslinks between NIPA chains, are effective at extracting cationic, amine-based solutes from aqueous solution. The cationic species are believed to adsorb on the anionic surfaces of the laponite particles within the gel. The separation efficiency of these hybrid gels for dyes such as MB is shown to be superior to that of commercial ion-exchange resins. We have also discovered a way to disassemble NIPA–LAP gels by exposure to solvents such as DMF, THF, and PEG. This approach allows the recovery of bound solute from within the gel. Additionally, by combining the thermoresponsive LCST behavior of NIPA–LAP gels in conjunction with solvent-induced disassembly, we have demonstrated an approach for concentrating and recovering the bound solute.

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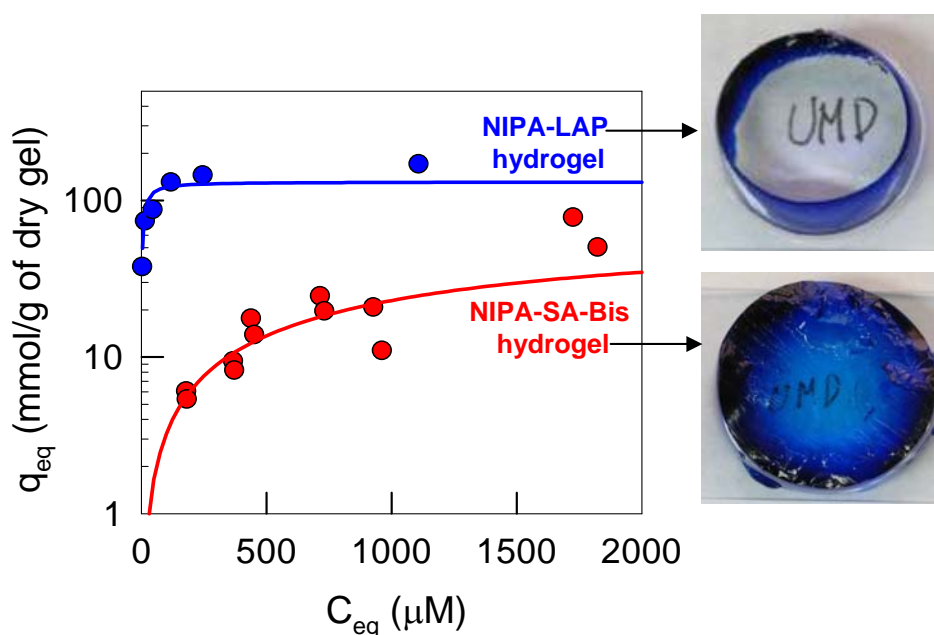
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## Supporting Information for

### Nanoparticle-Crosslinked Hydrogels as a Class of Efficient Materials for Separation and Ion Exchange

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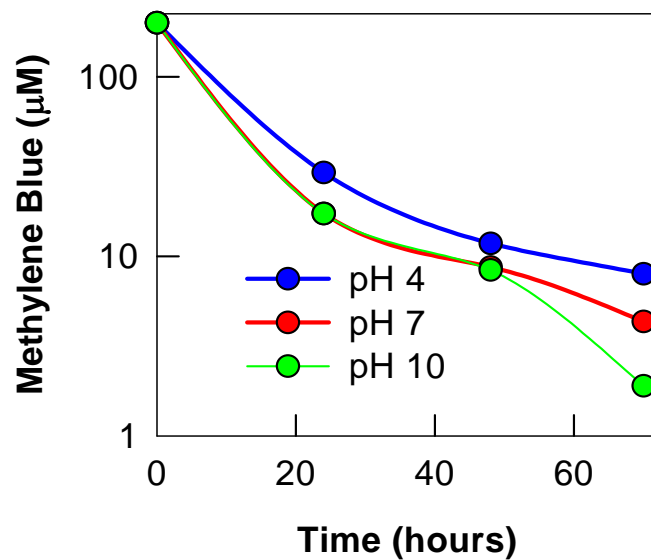


**Figure S1.** Adsorption isotherms for a NIPA-laponite hydrogel and a NIPA-SA-BIS hydrogel in solutions of the cationic dye, methylene blue (MB). The plot shows the equilibrium adsorbed amount of dye per gram of dry gel ( $q_{eq}$ ) as a function of the equilibrium dye concentration  $C_{eq}$  in solution. The lines through the data are fits to the Langmuir adsorption isotherm (eq below).  $q_{max}$  is the maximum possible amount of dye that can be adsorbed and  $b$  is the adsorption constant. Fitted parameters are shown in the table below. Cross-sections of the two gels are shown by the photographs. Note that the dye is confined to a thin layer near the surface in the case of the NIPA-laponite gel whereas it is distributed uniformly in the case of the NIPA-SA-BIS gel.

Langmuir equation:

$$q_{eq} = \frac{q_{max} \cdot b \cdot C_{eq}}{1 + b \cdot C_{eq}}$$

gel type	$q_{max}$ ( $\mu\text{mol/g}$ )	$b$ (1/mM)
NIPA-Laponite	132.4	0.121
NIPA-Sodium Acrylate-BIS	71.9	0.00047



**Figure S2.** Separation of the cationic dye, methylene blue (MB), from buffered solutions of different pH by a laponite-crosslinked NIPA gel. Plots of dye concentration vs. time are shown for three different pH values. The results are nearly identical, indicating that the binding of MB to laponite is unaffected by pH.