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Poly (*N*-Isopropylacrylamide) Microgels for Organic Dye Removal from Water

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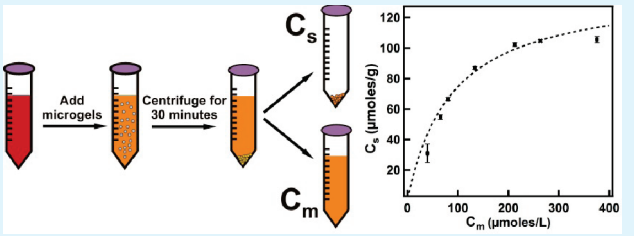
Supporting Information

ABSTRACT: The ability of poly (*N*-isopropylacrylamide) (pNIPAm), and pNIPAm-*co*-acrylic acid (pNIPAm-*co*-AAc) microgels to remove an organic azo dye molecule, 4-(2-Hydroxy-1-naphthylazo) benzenesulfonic acid sodium salt (Orange II) from aqueous solutions at both room and elevated temperature was assessed. At room temperature, we found that the amount of Orange II removed from water (removal efficiency) increased with increasing AAc and microgel concentration. The removal of Orange II from water was also fit by a Langmuir sorption isotherm model. Furthermore, we found the extent of Orange II removal depended on solution temperature; more Orange II was removed from water at elevated temperature and as the microgels were held at that temperature for longer durations of time. Additionally, by increasing the cycles between high and ambient temperature, the removal of Orange II was enhanced, although this was only true for two temperature cycles. We hypothesize that this is a result of the thermoresponsive nature of pNIPAm-based microgels which deswell at elevated temperature expelling their solvating water and when the microgels are cooled back down they reswell with the Orange II containing water. We also hypothesize that the microgels become saturated after the second heating cycle and so the efficiency of removal did not increase further. Finally, we assessed the ability of the microgels to retain the Orange II after it is removed from the aqueous solution. We determined that the microgels "leak" 25.6% of the Orange II that was originally removed from the water.



KEYWORDS: water remediation and contamination, poly (*N*-isopropylacrylamide) microgels, thermo responsive materials, azo dyes, NIPAm

INTRODUCTION

Azo dyes are a class of organic compounds that are used as colorants in textile, cosmetics, food and drug industries.[1] Azo dye containing effluents from these industries has been a major cause for concern, especially in developing countries, due to their ability to transform into carcinogenic aromatic amines.[1] Additionally, these dyes have been shown to be directly toxic to both human and aquatic life. The textile industry alone uses several thousand different dyes, out of which about 30% are classified as reactive dyes. Reactive dyes have functional groups, for example, azo, anthraquninone, oxazine that get activated and react with the fibres of the dyable material. Of these, azo dyes comprise nearly 60% of these reactive dyes, and are mainly employed by the textile industry due to their bright color.[2] Many physicochemical and biological methods have been used to remove several dyes from industrial effluents including membrane filtration, nanofiltration membranes, photo catalytic processes, and combined anaerobic−aerobic bacteria treatment.[3−6] While this is the case, the techniques are often costly, not easy to implement/maintain, and are not efficient.[7−11] In recent years, there have been various hydrogel based systems investigated for their ability to remove from water a variety of cationic and anionic dyes such as methyl violet, methylene blue.[12−15] In other studies, hydrogel composites and polyelectrolytes were explored for water remediation purposes.[16−20]

Relevant to this study are materials composed of responsive polymers. Responsive polymers are a class of polymers that respond to external stimuli by changing their physical and/or chemical state. Responsive polymers have been made to be sensitive to a variety of stimuli including: temperature, pH, ionic strength, light, force, and analyte concentration.[21−28] Arguably the most well studied responsive polymer is poly (*N*-isopropylacrylamide) (pNIPAm).[29−37] PNIPAm is fully water-soluble and is thermoresponsive, that is, it exists as a random coil in aqueous solution, but transitions to a compact globule conformation at $T > \sim 32$ °C, which is pNIPAm's lower critical solution temperature (LCST).[30,31,34,35] This transition is also accompanied by an dissociation of water from the polymer chain.

It is very well-known that colloidal particles can be synthesized from NIPAm.[30,31,33,35−39,38−41] These colloids, referred to as microgels, are water-soluble, highly porous, and thermoresponsive. That is, pNIPAm microgels decrease in diameter at $T > \sim 32$ °C, expelling their solvating water as a result, and reswell at $T < \sim 32$ °C. PNIPAm microgels have also been made to respond to a variety of stimuli, by addition of a functional monomer into the

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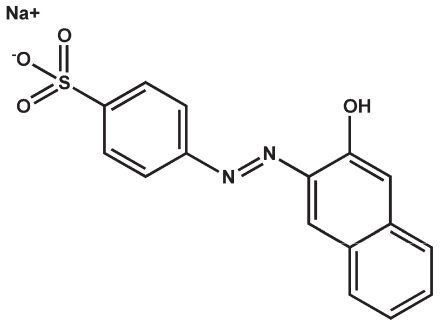

Figure 1. Chemical structure of Orange II.

synthesis as a comonomer.[33,36−39,42,43] Among the most common comonomer used is acrylic acid (AAc), which has a pK_a ∼ 4.25, which causes the microgel to swell at pH > pK_a, and hinders the thermoresponsivity due to Coulombic repulsion.[33,44−46]

Previously, hydrogels of pNIPAm modified with polyacryamide have been employed to determine the partition coefficient of Orange II and methylene blue in the system at different temperatures. It was reported that the permeability of Orange II through the hydrogels increased when temperature was raised above 32 °C.[47,48] PNIPAm hydrogels and microgels, and pNIPAm-co-methacrylic microparticles have been used in the past for removal of dyes like Nile red, brilliant green, brilliant cresyl blue, etc. and heavy metal ions like Pb (II) and Cu (II) for water treatment applications.[49−52]

In this submission, we assess the ability of thermoresponsive pNIPAm-*co*-AAc microgels to remove the azo dye molecule 4-(2-hydroxy-1-naphthylazo)benzenesulfonic acid sodium salt (Orange II) from water, Figure 1. While Orange II was chosen as a model azo dye molecule, and a model molecule for any number of potential organic contaminants found in water, Orange II itself has been considered as a water contaminant. For example, Orange II has been found in industrial effluents and has been treated using many chemical and physical techniques.[53−55] We assessed the uptake efficiency as a function of AAc and microgel concentration, and how the uptake changed as the temperature of the water was varied and the number of times the microgels were cycled above and below their LCST. We also determined the ability of pNIPAm microgels to retain the removed Orange II. We found the pNIPAm-*co*-AAc microgels to have a reasonable affinity for Orange II, removing 29.5% Orange II at room temperature, which was significantly increased to 56.6% upon heating. Additionally, the microgels are able to retain most of the Orange II that was initially removed from the water. The data obtained from these experiments will be used to guide our future efforts in water remediation, but will also serve as information for our efforts related to drug delivery.[56] For example, we are trying to identify microgel based systems that are able to retain small molecules, and release them in a temperature triggered fashion.

This study represents a comprehensive assessment of pNIPAm-based microgels for water remediation applications. Not only does the study reveal the important factors that need to be considered when using these systems for this application, but it also may have significant practical utility. For example, we achieve 56.6% uptake efficiencies after only 90 min of contact with the "contaminated" water, while other recently reported systems require many hours of contact time to approach the uptake efficiencies reported here. Additionally, the system here is able to retain the majority of the Orange II that is removed from the water. This fact will allow the microgels to be physically separated from the contaminated water by filtration, effectively remediating the water. Future studies of this system will involve tuning the pNIPAm-based microgel chemical functionality to specifically enhance the uptake efficiency for certain contaminants, while allowing for the contaminant molecules to be removed from the microgel structure through treatment after microgel isolation from the contaminated water. This then will allow the microgels to be applied and removed from the contaminated water, treated to remove the isolated dye from the microgel network, and subsequently reused for remediation. While this will be the topic of future investigations from the group, the studies here set the precedent for our future work. The current study hence highlights an inexpensive, straightforward, and efficient method for removing azo dyes from aqueous solutions with extensive future utility.

MATERIALS AND METHODS

Materials. The monomer, *N*-isopropylacrylamide was purchased from TCI (Portland, Oregon) and purified by recrystallization from hexanes (ACS reagent grade, EMD, Gibbstown, NJ). *N*,*N*′-methylenebisacrylamide (BIS) (∼99%), acrylic acid (AAc) (∼99%), and ammonium persulfate (APS) (∼98%) were obtained from Sigma-Aldrich (Oakville, Ontario) and were used as received. Orange II was obtained from Eastman Organic Chemicals (Rochester, New York). All the phosphate salts used for preparing buffer solutions of pH 7 and pH 3, with ionic strengths of 0.235 and 0.09 M, respectively, were obtained from EMD and were used as received. Deionized (DI) water with a resistivity of 18.2 MΩ · cm was obtained from a Milli-Q Plus system from Millipore (Billerica, MA), and filtered through a 0.2 μm filter, prior to use. Microgel samples were lyophilized using a VirTis benchtop K-manifold freeze-dryer (Stone Ridge, New York)

Synthesis of Microgels. Microgels composed of poly (*N*-isopropylacrylamide) were prepared by a surfactant free, free radical precipitation polymerization as described previously.[32] The total monomer concentration was 140 mM, and was 95% *N*-isopropylacrylamide (NIPAm) and 5% *N*,*N*′-methylenebisacrylamide (BIS) cross-linker. The monomer, NIPAm (13.3 mmol), and the cross-linker, BIS (0.700 mmol), were dissolved in deionized water (75 mL) with stirring in a small beaker. The mixture was filtered through a 0.2 μm filter affixed to a 20 mL syringe into a 250 mL, 3-neck round-bottom flask. An additional aliquot of deionized water (24 mL) was used to wash the beaker, which was filtered and transferred to the round-bottom flask. The flask was then fitted with a thermometer, a condenser, stir bar, and a N_2 inlet. The temperature was set to 65 °C and N_2 was bubbled through the solution for ∼1 h, after which 0.197 mmol of 1 mL aqueous solution of APS initiator solution was added to the reaction mixture and was left to stir in the flask for 4 h, under N_2 atmosphere. The solution was allowed to cool, while stirring overnight.

Microgels composed of pNIPAM-*co*-AAc were prepared in a similar way by adding 0.700 mmol, 1.40 and 2.10 mmol of AAc to the reaction mixture to synthesize pNIPAm-*co*-AAc microgels that were 5%, 10%, and 15% AAc, respectively. The AAc was always added just prior to initiation, and the concentration of NIPAm was adjusted accordingly to maintain the monomer/cross-linker concentration constant at 140 mM for all microgel syntheses. The %AAC in the microgels will be represented as pNIPAM-*co*-XAAc, where X = 0, 5, 10, and 15% AAc. The diameters of these microgel systems were determined using dynamic light scattering using a ALV/CGS-3 Compact Goniometer System (Hesse, Germany) and were calculated as 795.4 nm, 945.2 nm, 1.103 and 1.384 μm for

pNIPAm-*co*-XAAc where X = 0, 5, 10, and 15%, respectively (see Supporting Information).

Following stirring overnight, all microgels were filtered through a type 1 Whatman filter paper, which was then rinsed with deionized water. To remove unreacted monomer and cross-linker, as well as linear polymer from the microgels, the microgel reaction solution was separated into 15 mL centrifuge tubes obtained from Corning Incorporated (Corning, NY) (~ 12 mL microgel solution/tube) and centrifuged at a speed of ~8400 relative centrifugal force (rcf) in a Baxter, biofuge 17R (Mount Holly, NJ) at 23 °C, for 30 min. Centrifugation yielded a pellet of microgels at the bottom of the centrifuge tube, and the supernatant was removed. ~12 mL of fresh DI water was added and the microgel pellet was redispersed using a Fisher Vortex, Genie 2 vortexer (Pittsburgh, PA). This cleaning protocol was repeated six times.

Orange II Uptake. Microgels were lyophilized, and 52.1 mg of each was redispersed in 10 mL of pH 7 buffer solution of 0.235 M ionic strength in a volumetric flask. The concentration of the stock microgel solution was 5.21 mg microgels/mL. A stock solution of 0.023 M Orange II in deionized water was prepared. Using a micropipet, 300 μL of microgels and 15 μL of Orange II were transferred into a 15 mL centrifuge tube obtained from Corning Incorporated (Corning, NY). A buffer solution of pH 7 of ionic strength 0.235 M was added to the tube to give a total volume of 3 mL (final concentrations of microgels and Orange II are 521 μg/mL and 114 μM, respectively). For all the experiments the buffer was added only after the dye was exposed to the microgels. This solution was allowed to sit for five minutes and then centrifuged for 30 min, at ~8400 rcf to pack the microgels at the bottom of the centrifuge tube. This centrifugation time was used to ensure that all the dispersed microgels were removed from solution (as confirmed from differential interference contrast microscopy, data not shown). The supernatant was carefully removed from the tube without disturbing the microgel pellet at the bottom of the centrifuge tube and transferred to a quartz cuvette and the absorbance measured using a HP8452A UV−vis spectrophotometer with a diode array detector (previously Agilent Technologies, Inc., Santa Clara, CA). The initial concentration of Orange II for all the uptake studies was maintained at 114 μM and it was also observed that the pH of Orange II solution does not change when microgels are added to it. The initial absorbance of Orange II without microgels was also measured as a function of time the solution stayed in the tube. It was confirmed that the tube did not have any effect on increasing/decreasing the absorbance of Orange II, independent of time.

Similar studies were performed at room temperature, using a buffer solution of pH 3 with an ionic strength of 0.09 M. To study the uptake of Orange II as a function of temperature, the solution of Orange II and microgels (only with pH 7 buffer solution) was held at 50 °C, for different intervals of time (microgels deswell) and then cooled down to room temperature (microgels reswell). This solution was then centrifuged and the supernatant was used to perform UV−vis studies.

Orange II Leaking Studies. To evaluate the ability of the microgels to retain Orange II, the concentrations, and volumes from the previous section were scaled up three times. So in this case, 900 μL of microgels were exposed to 114 μM Orange II in a total volume of 9 mL using the same buffer that was used for the uptake studies. This scaling up was done to get a detectable absorbance signal from the solutions after leaking. As for the Orange II removal studies above, the solution was allowed to sit for five minutes followed by centrifugation for 30 min. The supernatant solution was then carefully removed without disturbing the microgels packed at the bottom. To this tube, 9.0 mL of fresh buffer solution (the same buffer that was used for the uptake studies) was added and then the microgels were redispersed by vortexing. This was immediately divided into nine, one mL samples in 1.5 mL Eppendorf tubes obtained from Fisher Scientific, (Ottawa, ON) and the solutions were allowed to incubate for various intervals of times. For example, immediately following splitting up the original solution, one tube was centrifuged for 30 min and the supernatant solution removed and UV−vis performed on the supernatant solution, this was considered t = 0. We allowed the other tubes to incubate for 10, 20, 30, 40, 50, 60, 80, and 100 min, respectively, before each was centrifuged.

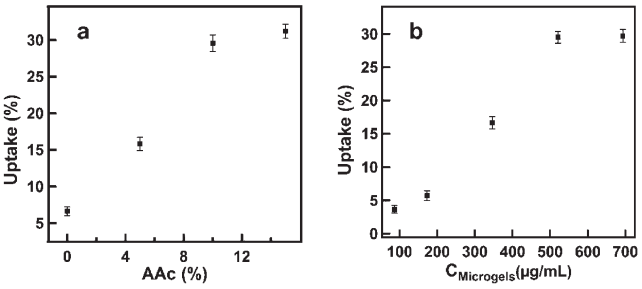

Figure 2. Uptake of Orange II as a function of (a) percentage of AAc (0%, 5%, 10% and 15%) present in the pNIPAm microgel system and (b) concentration of pNIPAm-*co*-10AAc. All the solutions were in a total volume of 3 mL and pH 7 buffer. Each point on the plots represents an average of three replicate experiments of uptake studies and the error bars denote the standard deviation.

RESULTS AND DISCUSSION

Uptake Studies at Room Temperature. The ability of microgels to remove organic azo dyes from aqueous solutions of pH 7 with ionic strength of 0.235 M was investigated by exposing them to Orange II. Initially, we investigated the effect of adding the weak acid AAc to the microgel structure. The experiment was performed by recording an initial absorbance spectrum of 114 μM Orange II before the addition of 300 μL of microgels (521 μg/mL), and comparing that to the absorbance of the supernatant after the addition of microgels. If Orange II was removed from the solution a decrease in absorbance will be observed. The number of moles in the solution before and after microgel addition was determined using a calibration curve (see Supporting Information). The percent of Orange II removed from the solution was subsequently calculated. Figure 2(a) shows the percent uptake as a function AAc concentration in the microgels. The percent uptake was found to depend critically on the AAc concentration, increasing from 6.63% for the pNIPAM-*co*-0AAc to 31.2% for pNIPAM-*co*-15AAc microgels. This trend could be due to the increase in the size of the microgels as the %AAc increases, as determined by DLS, where the size of the microgel increased from 795.4 nm for pNIPAm-*co*-0%AAc to 1.384 μm for pNIPAm-*co*-15AAc. The uptake percent using pNIPAm-*co*-10AAc was 29.5% (only about 2% less than the 15% AAc system) and these microgels were used for subsequent experiments. Removal efficiency of microgels in pH 3 aqueous solution with an ionic strength 0.09 M was also investigated using the same protocol as above. It was observed that the change in pH did not significantly alter the removal efficiency of the dye (see Supporting Information). While this is the case, we chose to maintain the pH of the solutions at 7 for all other studies.

The effect of microgel concentration on the removal efficiency was also investigated, and the results are depicted in Figure 2(b). The removal efficiency steadily increased from 3.60% to 29.5% as the amount of pNIPAM-*co*-10AAc microgels was increased

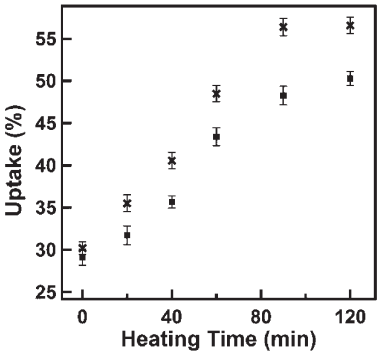

Figure 3. Uptake of Orange II as a function of the time the microgels were held at elevated temperature for (■) one and (x) two cycles. Each point on the plot represents an average of three replicate experiments of uptake studies and the error bars denote the standard deviation.

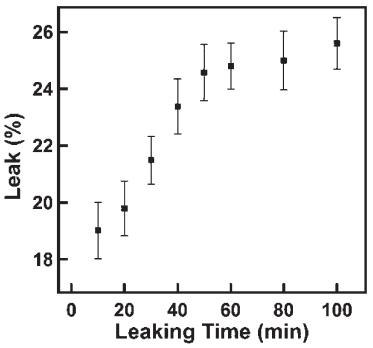

Figure 4. Leaking of Orange II from 10% AAc microgels as a function of leak time. Each point on the plot represents an average of three replicate experiments of leaking studies and the error bars denote the standard deviation.

(86.6, 173, 346, and 521 μg microgels/mL), but did not increase for 693 μg microgels/mL). We hypothesize that this behavior is observed because the removal of dye is an equilibrium process and addition of more microgels to the solution, past a certain concentration, will not result in extra moles of the dye being removed.

Removal Efficiency As a Function of Temperature. *1. Single Heating and Cooling Cycle of Microgels.* PNIPAm microgels are well-known to be thermoresponsive. That is, at $T >$ ~32 °C they decrease in diameter by expelling their water of solvation, as result they become more hydrophobic. This process is reversible, so at $T <$ ~32 °C the microgels rehydrate and return to their initial state. At this pH and ionic strength, the thermoresponsivity was still observed, as confirmed from light scattering experiments (see Supporting Information).

For the uptake studies, we exposed 300 μL (521 μg/mL) pNIPAM-*co*-10AAc microgels to 15 μL of Orange II, and cycled the temperature above and below 32 °C and calculated the percent removal. We hypothesize that when the microgels rehydrate, they will absorb excess Orange II from solution. Additionally, we characterized the uptake efficiency as a function of time that the microgels were held at an elevated temperature. Specifically, the microgels were exposed to Orange II for five minutes and heated to 50 °C for periods of 20, 40, 60, 90, and 120 min. The solution was immediately cooled to room temperature (~23 °C) for 30 min and centrifuged. The absorbance of the supernatant solution was then evaluated and percent removal determined. Figure 3 shows that the percent of Orange II removed from solution increased from 29.5% (at RT) to 50.3% as the time the solution was held at elevated temperature increased to 120 min. The figure also suggests that no more dye is taken up after the 90 min heating and 30 min cooling experiment. A control experiment was performed by heating Orange II of the same concentration (in buffer) in the absence of microgels. It was shown that the absorbance intensity of Orange II decreased by only 3.5% due to heating alone (see Supporting Information), which confirms that the improved uptake efficiency of the microgels by heating was indeed due to the thermoresponsive nature of the microgels.

2. Multiple Heating and Cooling Cycles of Microgels. Results from the previous section indicate that temperature affects the removal efficiency of the microgels, which is hypothesized to be due to the thermoresponsive nature of the microgels. The effect of multiple heating cycles was also investigated. This was done by heating 300 μL (521 μg/mL) of pNIPAM-*co*-10AAc microgels exposed to 15 μL of Orange II to 50 °C two times, followed by cooling cycles. The heating times were chosen such that the total time the microgels were held at elevated temperature matched the times for the single cycle, the only difference being the number of times the microgels were heated and cooled. For example, a solution of microgels was exposed to Orange II for five minutes, brought to 50 °C for 10 min, cooled for 15 min, heated again for 10 min, followed by cooling for 15 min. Overall, the microgels were at elevated temperature for 20 and at RT for 30 min, equivalent to the microgels that were heated 1 time for 20 min. This was repeated for all the single cycle heating times. Figure 3 shows that the uptake of Orange II increased after an additional heating cycle. The maximum uptake was increased from a maximum of 50.3% from one hot cycle to 56.6% for an extra hot cycle. The uptake also levels off after 90 min, similar to the single hot cycle data. We also investigated the effect of the cycling the temperature one more time, and did not observe a significant increase in in the removal efficiency (see Supporting Information).

Leaking Studies of Orange II. While the maximum removal efficiency of the microgels was shown to be ~56.6%, with two 45 min heating cycles, it is important to evaluate the ability of the microgels to retain the Orange II that was removed from the water. To evaluate this, we exposed 900 μL of pNIPAm-*co*-10AAc to Orange II for five minutes in a total volume of 9 mL using the same buffer as in the uptake studies, and the solution was centrifuged and the supernatant solution removed. The resulting microgel pellet was redispersed in 9 mL of fresh buffer by vortexing and divided into nine different Eppendorf tubes and allowed to incubate for various time intervals, from 0 to 100 min and then centrifuged, as indicated in the Materials and Methods section. The supernatant solution was then evaluated and the percent Orange II leaked calculated. The percentage of Orange II that was leaked was determined by calculating the number of moles Orange II that was initially removed from the solution and then determining how much was expelled after a given incubation time interval. The concentrations of Orange II were determined from a calibration curve, as indicated above. For example, the "0 min" sample was immediately centrifuged after splitting the solution up and the supernatant solution evaluated. The number of moles in this solution was compared to how many moles were initially in the microgels. Figure 4 shows the trend for the percent leaking of Orange II as a function of leaking time.

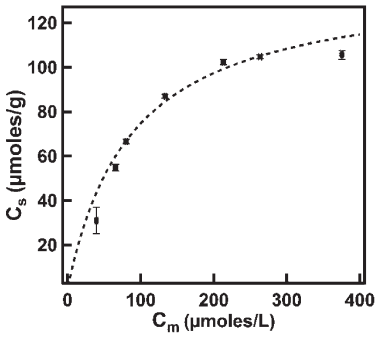

Figure 5. Langmuir adsorption isotherm for the removal of Orange II by the microgels. *Cm* is the concentration of the dye remaining in the aqueous phase and Cs is the concentration of the dye sorbed to the microgels. The goodness of fit (R^2) value was calculated as 0.9518. Each point on the plot represents an average of three replicate experiments and the error bars denote the standard deviation.

The figure indicates that percentage of Orange II that leaked from the microgels increased with time up to 50 min and leveled off after this time. We calculated that a maximum of 25.6% of the absorbed dye leaks out of the microgels. This translates to a 74.4% retention efficiency. We also addressed the possibility of Orange II leaking out further with the addition of fresh buffer. We removed the supernatant from the sample that was allowed to incubate for 100 min and added 1.0 mL fresh buffer to this system and allowed the solution to incubate for 60 min. This was then centrifuged and the supernatant was removed to record the absorbance; no significant increase in leaked Orange II was observed. Additionally, we studied the possibility of microgels leaking out Orange II at elevated temperature. The microgels deswell by expelling water of solvation when heated above their LCST. In order to test if the microgels leak out more Orange II at higher temperatures, we redispersed the supernatant from the tube that was allowed to incubate for 100 min (at room temperature) with the microgels. This solution was then allowed to incubate for another 100 min on a hot plate at 50 °C and was immediately centrifuged for 30 min at 50 °C by regulating the thermostat in the centrifuge. The supernatant was removed and the absorbance was measured. The results show that leaking is not affected by temperature, see Supporting Information.

Uptake Studies As a Function of Orange II Concentration. We also investigated the ability of the pNIPAm-*co*-10AAc microgels to remove Orange II from aqueous solution as a function of Orange II concentration. We exposed 300 μL (521 μg/mL) of pNIPAM-*co*-10AAc microgels to 5, 10, 15, 20, 25, 30, and 35 μL of Orange II from the stock solution in a total of 3 mL buffer (pH 7, 0.235 M ionic strength). The microgels were then centrifuged for 30 min and the supernatant was analyzed by UV−vis, as explained above. The data (Figure 5) was fit with a Langmuir isotherm (eq 1), which yielded a maximum concentration of Orange II adsorbed on the microgels as 139.9 μmol/g (0.049 g Orange II/g microgels) and a Langmuir coefficient of 0.01143 ± 0.00134 g/μmoles was calculated.

$$C_{i,s} = C_{i,smax} \times K_{ads} \times C_{i,m}/(1 + K_{ads} \times C_{i,m}) \qquad (1)$$

where $C_{i,s}$ is the concentration of the dye in sorbent (microgels); $C_{i,m}$ is the concentration of the dye in the mobile phase (in buffer after centrifugation); K_{ads} is the Langmuir coefficient

There are reports of pNIPAm microgels and other polymer systems that adsorb certain organic molecules in a Langmuir adsorption pattern.[57,58] The R^2 value was calculated as 0.9518, which indicates that Langmuir model is a reasonable one to use.

CONCLUSION

We report microgel systems of pNIPAm modified with varying concentrations of AAc which efficiently absorb the azo dye Orange II, the most efficient of these systems being pNIPAm with 10%AAc. The results indicate that by exploiting the thermoresponsive nature of these microgels, the percent absorption of Orange improved significantly by heating and cooling the microgels for a single cycle when compared with room temperature studies. The control experiments performed prove that the decrease in absorbance was due to the uptake of Orange II by the microgels and not merely due to any change in the absorbance of Orange II at higher temperatures. Furthermore, the leaking studies show that the microgels leak out 25.6% of the Orange II that was originally removed from solution, with no more leaking occurring after 50 min. The Langmuir coefficient of 0.01143 ± 0.00134 was calculated by fitting a Langmuir isotherm to the data in Figure 5. In the future, we will use these systems to remove naphthenic acids, PAHs, PCBs, drug molecules, etc. present in the industrial effluents and of major concern for human and aquatic life. Also, we will use this information to design efficient drug delivery systems.

ASSOCIATED CONTENT

Supporting Information. UV−vis spectra for Orange II held at high temperature in the absence of microgels and leaking studies of Orange II at high temperature, calibration plot used for calculating the uptake efficiency, trend for uptake of Orange II as a function of AAc percentage at pH 7 and pH3, trend for uptake of Orange II for multiple (three) heating and cooling cycles, light scattering data for thermoresponsivity of the microgels and DLS data for the different sizes of the microgels. This material is available free of charge via the Internet at http://pubs.acs.org.

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