Recyclability of Poly (*N*-Isopropylacrylamide) Microgel Based Assemblies for Organic Dye Removal from Water

*Deepika Parasuraman, Avijeet K. Sarker and Michael J. Serpe**

Department of Chemistry, University of Alberta, Edmonton, AB, T6G 2G2

[*] To whom correspondence should be addressed: (michael.serpe@ualberta.ca)

Abstract

Poly (*N*-isopropylacrylamide)-co-acrylic acid (pNIPAm-*co*-AAc) microgels and their aggregates have been shown to effectively remove organic dye molecules from aqueous solutions. Here, we investigate the reusability of these microgel-based systems by exposing them to the organic azo dye molecule, 4-(2-Hydroxy-1-naphthylazo) benzenesulfonic acid sodium salt (Orange II). Following exposure, the microgels are isolated, and added to methanol to extract the trapped Orange II from the microgels, followed by a subsequent isolation. The isolated microgels were then exposed to Orange II once again, and the uptake efficiency of the recycled microgels determined. We found that the microgels and their aggregates could be reused to remove the organic dye with little loss in extraction efficiency with the number of recycling cycles.

Introduction

Recent statistics reveal that there are close to 1 billion people in the world who do not have access to potable drinking water and more than a billion who lack access to adequate water sanitation facilities.[1] This has driven the demand for improved techniques to treat wastewater to provide pure and clean water that is free from harmful chemicals and pathogens.

Various inorganic, organic and biological impurities can be found in untreated water. The sources of these contaminants are both natural and anthropogenic. For instance, naturally present inorganic constituents (1.0 to 1000 mg/mL) in water include calcium, magnesium, potassium, bicarbonate, chloride, sulphate and nitrate.[1] Contaminants in water due to human activities include copper, arsenic, silver, mercury, zinc, chromium, and nickel.[1, 2-6] Heavy metal ions including arsenic, zinc, mercury and chromium are also found naturally (0.01 to 10 mg/L) due to rock weathering and leaching from soil/sediment. Organic contaminants from natural sources are called natural organic matter (NOM), formed as a result of chemical and microbial degradation of vegetation. [7-9] Sources of synthetic organic compounds (SOCs) include industries, careless disposal of chemical waste in landfills and various other commercial activities. [10,11]

Several water treatment techniques have been reported over the past decade. The most common of these include chemical precipitation (coagulation/flocculation), adsorption, ion-exchange, membrane filtration, electrochemical treatments, and approaches using nanomaterials.[12-24] These methods have been used extensively for removal of heavy metal

ions, [12-15] organic contaminants such as antibiotics, [16-18] herbicides,[19-21] polychlorinated biphenyls (PCBs), poly and aromatic hydrocarbons (PAHs).[22-24]

Polymers are widely used in the water remediation industry; while this is the case, we will focus on highlighting water remediation approaches using poly (*N*-isopropylacrylamide) (pNIPAm). [25-29] PNIPAm is fully water soluble, and thermoresponsive, i.e. it exists as a random coil in water at T < ~32 ˚C and transforms to a globule conformation by expelling much of its solvating water at T > ~32 ˚C.[30-38] The temperature at which this occurs at is called the lower critical solution temperature (LCST). [31,32,35,36] PNIPAm-based colloids (microgels) can also be synthesized to yield highly porous, and water soluble/swellable structures. [31,32,34,36,39-42]While the microgels are hygroscopic, they also exhibit hydrophobic properties.

PNIPAm-based microgels are typically synthesized using free-radical precipitation polymerization.[34,37-40, 43, 44] Using this synthetic route, various chemical functionalities can be easily added to the microgels via copolymerization.[34,37,40] These chemical functionalities can render the microgels responsive to various stimuli. [45-52] Furthermore, the added chemical functionality can cause the microgels to interact with specific small molecules of interest for water remediation applications. The most common comonomer employed for this purpose is acrylic acid (AAc), which has a pK_a ~ 4.25. Therefore, at pH > pK_a, the microgels swell due to Coulombic repulsion in the microgel network. This property also hinders the thermoresponsivity of pNIPAm-*co*-AAc microgels. [34, 53-56]

PNIPAm based hydrogels and microgels have been used in applications such as removal of heavy metal ions like Pb (II) and Cu (II) and dyes like Nile red, brilliant green, and brilliant cresyl blue. [25-28] Furthermore, Snowden and co-workers studied the use of colloidal pNIPAm

microgels for the absorption of heavy metal ions from aqueous solutions.[29] They suggested that microgel absorption properties are dependent to a certain extent on the form of charged functional groups (anionic or cationic) that are present on the surface of a microgel particle. In their study, they found that after 6 hours at 25°C in pH 6 solution, cationic microgel particles had a larger capacity to absorb lead nitrate than anionic microgels. Cationic pNIPAm microgel particles adsorbed ~35mg/g of lead nitrate, while anionic pNIPAm microgel particles absorbed ~10 mg/g of lead nitrate. It was also determined that cationic pNIPAm microgels had a higher maximum uptake rate (0.52 mg g^{-1} min^{-1}) than the anionic microgel analogue (0.12 mg^{-1} min^{-1}). Despite differential analyte uptake between these cationic and anionic pNIPAm microgel species, it was found that upon heating to 50°C for 3 hours, both microgel particles re-released ~60% of the initially adsorbed lead nitrate species. Subsequent secondary re-absorption cycles on previously saturated cationic microgels yielded absorption behavior that was comparable to the original values 35mg/g), indicating a potential for reusability.

In our previous work, we established that pNIPAm-*co*-AAc microgels and their assemblies (aggregates) could be used to remove the organic azo dye molecule, 4-(2-Hydroxy-1-naphthylazo) benzenesulfonic acid sodium salt (Orange II) from water.[57-60] It was observed that the removal of dye by unaggregated microgels critically depended on the: 1) the % AAc, 2) temperature of solution, 3) diameter of the microgels, and 4) concentration of microgels present in the solution. We established previously that at room temperature 1.1 µm diameter microgels (pNIPAm-*co*-AAc-2, medium) and 1.43 µm diameter microgels (pNIPAm-*co*-AAc-3, large) removed 29.5% and 38.0% of Orange II from solution, respectively.[57-60] Furthermore, we previously established that the uptake from aggregated from pNIPAm-*co*-AAc-1 (small), pNIPAm-*co*-AAc-2 (medium) and pNIPAm-*co*-AAc-3 (large) microgels critically depended on

the % AAc, solution temperature, aggregate concentration and diameter of microgels. In addition, the uptake also depended on hydrophobicity and size of the aggregates. In our previous reports, we established that the small, medium and large microgel aggregates originally removed 39.6%, 44.2% and 52.1% of Orange II from water, respectively.

In this study we perform similar Orange II uptake experiments to calculate an "uptake efficiency" of recycled microgel systems. We define the uptake efficiency as ((Orange II removed by recycled microgels or microgel-based aggregates)/(Orange II initially present in the aqueous dye solution) x 100). To recycle the microgels/aggregates, we used methanol (MeOH) to extract the dye that was initially taken up by them. The "extraction efficiency" was calculated as ((Orange II removed by methanol)/(Orange II removed by the microgels from the initial uptake) x 100). MeOH was chosen simply because the solubility of Orange II in MeOH is favorable. We acknowledge that the presence of MeOH can change the LCST of the microgels, but the influence of MeOH:water ratio on the extraction efficiency was not investigated as part of this study. We also point out here that we did not notice any aggregation of the microgels after the extraction process. The uptake efficiency for the "recycled" microgels was then determined after a given number of extraction cycles. That is, the Orange II was extracted from the microgels 1-5 times before they were re-exposed to another Orange II solution. We observed an increase in the uptake efficiency with increasing number of MeOH extraction cycles. We report similar results are reported for pNIPAm-based microgel aggregates.

Experimental

Materials: 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 persulphate (APS) (~98%) were obtained from Sigma-Aldrich (Oakville, Ontario) and

were used as received. Orange II was obtained from Eastman Organic Chemicals (Rochester, NY) and methanol was (~99.8%) was obtained from Caledon (Georgetown, Ontario). The phosphate salts for preparing buffer solutions of pH 7 (ionic strength of 0.235 M) 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, NY).

Synthesis of pNIPAm-co-AAc-1 microgels (D_H ~321 nm): These microgels were prepared using a previously used protocol.[37] The overall monomer concentration was 65.2 mM (13.05 mmol), wherein, 85% *N*-Isopropylacrylamide (NIPAm, 11.1 mmol), BIS (0.652 mmol), and sodium dodecyl sulfate (SDS, 0.2 mmol) were added to 190 mL deionized water, previously filtered through a 0.2 μm filter. This solution was transferred into a 3-neck round bottom flask, fitted with a reflux condenser, nitrogen inlet, and a thermometer. The solution was purged with N_2 and allowed to heat to 70 °C for ~1 hour. To this 10% AAc (1.30 mmol) was added in one aliquot immediately prior to initiation. APS (0.3 mmol) in 10 mL of DI water was added to the monomer solution for initiation. The reaction was allowed to proceed at 70 °C for 4 hours under a nitrogen atmosphere. The resulting suspension was allowed to cool overnight, and then it was filtered through a type 1 Whatman filter paper to remove any large aggregates. About half of the microgel solution was then distributed into rehydrated dialysis tubing (12-14k nominal MWCO, 25 mm flat width, Fisherbrand Regenerated Cellulose, Nepan, ON) for purification. The tubes were placed into two 2 L beakers with deionized water and a stir bar for two weeks

and the water was replaced twice daily. Dialysis was used to remove unreacted monomers and crosslinker, and small molecular weight linear polymers, from the microgels. Dynamic light scattering studies (data not included) using a ALV/CGS-3 Compact Goniometer System (Hesse, Germany) was used to determine the hydrodynamic diameter (D_H) of these microgels. PNIPAm-*co*-AAc-1 microgels were determined to have a D_H of 321 nm ± 9 nm.

Synthesis of pNIPAm-co-AAc-2 microgels (~ 1.1 μm): These microgels were prepared by a surfactant free, free radical precipitation polymerization as reported before.[34] The total monomer concentration was 140 mM. Of this, 85% was *N*-isopropylacrylamide (NIPAm), 5% was *N,N'*-methylenebisacrylamide (BIS) crosslinker and 10% was acrylic acid (AAc). To a clean beaker, NIPAm (11.9 mmol) and the crosslinker, BIS (0.700 mmol), were added and dissolved in deionized water (75 mL) in a beaker with stirring. A 20 mL syringe affixed with a 0.2 μm filter was used to filter the mixture into a clean 250 mL, 3-neck round bottom flask fitted with a condenser, thermometer, stir bar and a N_2 inlet. The beaker was rinsed with 24 mL of deionized water, which was again filtered and transferred to the mixture in the round bottom flask. The temperature was set to 65˚C with N_2 bubbling through the solution for ~ 1 h, after which AAc (1.4 mmol) was added to the mixture and stirred for a few minutes. To this, 0.197 mmol APS in 1 mL DI water was added. The mixture was allowed to stir for 4 h, under N_2 atmosphere. The solution was allowed to cool, while stirring overnight.

Following stirring overnight, the microgels were filtered through a type 1 Whatman filter paper, which was then rinsed with deionized water. The microgels were then cleaned via centrifugation to remove unreacted monomer and crosslinker, as well as linear polymers.

To do this, the microgel 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. The D_H of these microgels was determined by dynamic light scattering to be ~1.10 μm.

Synthesis of pNIPAm-co-AAc-3 microgels (Diameter ~1.43 μm): These were synthesized following a previously reported procedure.[61] The total monomer concentration was 153.8 mM (20 mmol) and 85% *N*-Isopropylacrylamide (NIPAm, 17.0 mmol), 5% *N*, *N'*-methylenebisacrylamide (BIS, 1.00 mmol) were added to 100 mL of deionized water in a small beaker and stirred. Once dissolved, the solution was filtered through a 0.2 μm filter into a 3-neck round bottom flask. The beaker was rinsed with 25 mL of deionized water and filtered into the flask. The flask was fit with a condenser, a nitrogen inlet, and a temperature probe to provide heating via a feedback-loop controlled hotplate (Torrey Pines Scientific, Carlsbad, CA). The flask was heated in an oil bath to 45 °C while the solution was allowed to stir and purge with N_2 gas for ~1.5 hours. Once the solution reached the set temperature, acrylic acid (AAc, 2.00 mmol, 10% of overall monomer concentration) was added followed by initiation of the reaction by addition of 0.078 M aqueous solution of ammonium persulphate in 5 mL DI water (overall solution volume resulted in 130 mL). After initiation, the reaction solution was then heated at a rate of 30 °C/hour to 65 °C and the reaction was allowed to proceed overnight under nitrogen

atmosphere. The resulting suspension was allowed to cool to room temperature, followed by filtration through a plug of glass wool to remove any coagulum formed during the reaction. The microgels were then cleaned via the same protocol as mentioned in the previous section. A diameter of ~1.430 μm was determined by microscopy as detailed in the previous section.

Synthesis of microgel aggregates: For the current study, we synthesized microgel aggregates using only one concentration of BIS -- 500 mg (10 mg BIS/mL of total reaction solution). These aggregates were prepared by directly adding 10 mL of cleaned microgels from the above syntheses to a filtered solution (filtered through 0.2 μm filter affixed to a 20 mL syringe) of 500 mg of BIS in 39 mL of deionized water, to a beaker and stirred. This solution was transferred into a 250 mL 3-necked round bottom flask that was fit with a condenser, thermometer, 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 1 h, a 1 mL aqueous solution containing 0.0175 mmol of APS was added to this mixture and left to stir for 4 h, under N_2 atmosphere. The solution was allowed to cool with stirring overnight. The microgel aggregates were cleaned using the same centrifugation procedure followed above for cleaning microgels, but without filtration.

Orange II uptake: All uptake studies were performed as outlined in our previous reports.[57-60] The uptake studies were performed prior to reusability studies, and the values of uptake were found to be similar to that of our previous reports. The first set of uptake studies was performed by using pNIPAm-*co*-AAc-2 (medium) and pNIPAm-*co*-AAc-3 (large) microgels, at room temperature. To do this, each of these microgel solutions were lyophilized and stock solutions were made from each sample to contain a concentration

of 5.2 mg /mL microgel solution. This was done by redispersing 52.1 mg microgels in 10 mL of pH 7 buffer solution of 0.235 M ionic strength in a volumetric flask. A stock solution of Orange II (0.023 M) in deionized water was prepared. Using a micropipette, 300 μL of the microgels and aggregate solution and 15 μL of Orange II were transferred into a 15 mL centrifuge tube (Corning Incorporated (Corning, NY)). A buffer solution of pH 7 (ionic strength 0.235 M) was used to bring the volume of the solution up to 3 mL yielding 114 μM Orange II and a final concentration of 521 μg microgels/ml of the reaction solution. After five minutes of exposure, this solution was centrifuged for 30 minutes, at ~8400 rcf. 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 pellet at the bottom of the tube and transferred to a quartz cuvette. The absorbance was 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 before every experiment, the initial absorbance of Orange II was measured in the absence of the microgels. The values of absorbance were determined using a calibration curve, which we could use to determine values to calculate removal and extraction efficiencies.

Uptake studies of pNIPAm-*co*-AAc-1 (small) microgels were not performed because the particles were too small in diameter to be centrifuged in a reasonable amount of time.

The second set of uptake studies was performed using aggregates of small, medium and large microgels, using 500 mg BIS (10 mg BIS/mL of total reaction solution). These studies were performed using the same protocol as outlined above, where the final

concentration of aggregates was maintained as 521 μg aggregates/ml of the reaction solution.

To study the uptake of Orange II by aggregates, as a function of temperature, the solution of Orange II and aggregates was held at 50 ˚C (microgels deswollen), for different intervals of time and then cooled down to room temperature (microgels reswell). The solutions were then centrifuged, and the supernatant was then analyzed by UV-Vis to evaluate the percent uptake of the dye,

Extraction studies: Methanol (MeOH) was used as the extracting solvent for these studies. Uptake studies were performed with medium and large diameter microgels, as detailed in the above section. The isolated microgels were then exposed to MeOH for five minutes followed by 15 minutes of shaking on a Fisher Vortex, Genie 2 vortexer (Pittsburgh, PA). The solution was again centrifuged for 30 minutes at ~8400 rcf. The supernatant was then transferred into a small glass vial and the methanol was evaporated using a rotary evaporator (Brinkmann Buchi RE-111, New Jersy, NJ). The dye on the walls of the vial was then redissolved in 3 mL of DI water. The number of moles of dye extracted was calculated using the absorbance measurements. using the calibration curve in Supporting Information. The microgels pellets were dried using the rotary evaporator to remove any methanol present in them before they could be reused. Scheme 1 illustrates this process.

The dried microgels were exposed to fresh dye solution and an uptake study was performed using the same protocol as outlined above. In order to do a subsequent extraction, another 3 mL of methanol was added to the dried microgels after the first extraction. These microgels were then redispersed in methanol and centrifuged in the

same way as mentioned above. For further extractions, the above sequence was repeated the desired number of times and then the uptake studies were performed on the dried microgels accordingly.

The extraction experiments for pNIPAm-*co*-AAc-1, 2 and 3 microgel-based aggregates were performed in a similar manner to the dispersed microgels, at room temperature. In addition, the dried aggregates were exposed to fresh solution of dye subsequent to the extractions and the solution was heated to 50 ˚C, for 90 minutes and cooled down to room temperature for 30 minutes before determining their uptake efficiencies.

Results and Discussion

Reusability studies on pNIPAm-co-AAc-2 and 3 microgels at room temperature: PNIPAm-*co*-AAc-2 and pNIPAm-*co*-AAc-3 microgels were first used to remove Orange II from aqueous solution. Following uptake, the microgels were isolated via centrifugation and their potential to be recycled was investigated. These experiments were all performed at room temperature. Briefly, the initial absorbance of a 3 mL solution of 114 μM Orange II was recorded in the absence of the microgels. This was then compared to the absorbance of the supernatant after addition of 300 μL of the microgels (from a stock solution containing 5.2 mg microgels/mL) to the same Orange II solution. The uptake efficiency for these microgels was determined to be 29.5% and 38.0% for the medium and large microgels, respectively, as reported in our previous work. [57-60] It should be pointed out here that these values are for reference only in this study. Therefore, we will compare the uptake efficiency of the recycled microgels to these reference values. To accomplish this, 3.0 mL of MeOH was added to the centrifuged microgels and allowed to incubate for 5 minutes. The microgels were then centrifuged,

and the resulting supernatant was transferred to a vial and the MeOH removed via rotoevaporation. 3 mL of fresh DI water was added to the vial and the number of moles of dye extracted after this step was determined by UV-Vis analysis and the extraction efficiency was calculated to be 72.5% and 71.2% for medium and large microgels respectively. The microgels packed at the bottom of the centrifuge tube were also dried using rotoevaporation to remove any methanol present in them and a subsequent uptake study was performed using the protocol detailed in the experimental. After one extraction, 20.9% and 30.2% uptake efficiency was achieved for medium and large microgels, respectively. In addition, we also studied the effect of increasing the number of extractions on the uptake efficiency. To do this, a series of experiments were performed where the uptake efficiency of the microgels after 2, 3, 4 and 5 extractions was evaluated. Figure 1 shows how the uptake efficiency changes with the number of extraction cycles the medium microgels undergo before being exposed to Orange II for a second uptake. It shows that as the number of extractions increases from 1 to 4, the uptake efficiency increased from 20.9% to 25.4% and upon increasing the number of extractions to 5, the efficiency increased only to 25.7%. Therefore, a maximum of 25.7% uptake can be expected from these microgels. The original removal efficiency of the medium microgels was a maximum of 29.5% at room temperature.[57] Figure 1 also shows the reusability of large microgels as a function of number of extractions. It shows that the uptake efficiency increased from 30.2% to 34.4% upon increasing the number of extraction from 1 to 4 and a maximum of 34.6% efficiency was achieved after 5 extractions. This is comparable to the original removal efficiency of 38.0% by the large microgels at RT. [59]

Reusability studies from pNIPAm-co-AAc-1, 2 and 3 microgels at room temperature: Initial uptake studies on pNIPAm-*co*-AAc-1 microgel aggregates were performed at room temperature using the protocol detailed in the experimental. Briefly, 300 μL of the 500 mg BIS aggregates of small, medium and large microgels were exposed to 15 μl of Orange II in pH 7 (0.235M ionic strength) in a 3 mL total volume. This solution was then centrifuged after five minutes and the absorbance of the supernatant was analyzed by UV-Vis. As reported before, the uptake efficiency was calculated to be 39.6%, 44.2% and 52.1% for the small, medium and large microgel aggregates respectively.[58-60] To study the reusability of these aggregates, the supernatant was discarded and 3 mL methanol was added to the aggregates and centrifuged. The supernatant from this sample was transferred into a vial and the methanol was evaporated using a rotary evaporator. To this vial, 3 mL DI water was added and the number of moles of Orange II present in the vial was determined by UV-Vis analysis. The extraction efficiency was determined to be 72.1%, 71.9% and 71.1% for small, medium and large microgel aggregates respectively. The aggregates were dried to remove any MeOH present in them, via a rotoevaporation. To this, fresh solution of Orange II was added and uptake studies were performed and monitored as a function of number of extractions. Figure 2 depicts the uptake efficiencies of small, medium and large microgel aggregates as the number of methanol extractions were increased from 1 to 5. Small microgel aggregates were determined to have an uptake efficiency of 28.7% after a single extraction and the uptake increased to 32.7% after 4 extractions. The uptake efficiency of medium microgel aggregates increased from 37.9% to 41.8% as the number of extractions increased from 1 to 4. For large microgel aggregates, after a single extraction, an uptake of 40.4% was achieved and increased to

47.5% after 4 extractions. For all these systems, there was no change in removal efficiency when the number of extractions was increased to 5.

Reusability studies on aggregates from pNIPAm-co-AAc-1, 2 and 3 microgels at elevated temperature: Initial uptake studies on all these systems were at elevated temperature as detailed in the experimental. Briefly, 300 μL of the 500 mg BIS aggregates of small, medium and large microgels were added to 15 μl of Orange II in pH 7 (0.235M ionic strength) in a 3 mL total volume, and heated the solution to 52 ˚C for 90 minutes and cooled down to room temperature for 30 minutes. This solution was then centrifuged immediately and the absorbance of the supernatant was analyzed by UV-Vis. The uptake efficiency was calculated to be 63.1%, 68.1% and 84.6% for the small, medium and large microgel aggregates respectively, as reported before.[59]

To study the reusability of these aggregates, the supernatant was discarded and 3 mL methanol was added to the aggregates and centrifuged. The supernatant from this sample was transferred into a vial and the methanol as evaporated using a rotary evaporator. To this vial, 3 mL DI water was added and the number of moles of Orange II present in the vial was determined by UV-Vis analysis. The extraction efficiency on each of these systems was calculated and is mentioned in the previous section. MeOH was removed from the aggregates by drying via a rotary evaporator. To this, fresh solution of Orange II was added to monitor the uptake efficiency at elevated temperatures as detailed before. The solution was heated to 52 ˚C for 90 minutes and then cooled back to room temperature for 30 minutes and this solution was immediately centrifuged and the supernatant was analyzed by UV-Vis. Figure 3 depicts the uptake efficiencies of each of

these systems as a function of number of methanol extractions. The uptake efficiencies were observed to increase from 58.7% to 60.2%, 60.6% to 63.4% and 74.2% to 77.6% for small, medium and large microgel aggregates, respectively, as the number of methanol extractions increased from 1 to 4. Similar to the room temperature studies, these systems did not show further removal of dye after 5 methanol extractions.

From the studies above, it is evident that our microgels and microgel-based aggregates can be recycled and reused for water remediation.

Conclusion

The reusability of microgels and microgel-based aggregates for water remediation was investigated. Methanol was used as the solvent to extract the original dye taken up by these systems. The reusability of these systems depended on the number of methanol extractions. At room temperature, it was observed that the unaggregated medium and large microgels removed a maximum of 25.7% and 34.6% of dye respectively, after 5 methanol extractions. This removal is fairly close to the original removal efficiencies of 29.5% and 38.0% for the medium and large microgels, respectively. For small, medium and large microgel-based aggregates, the reusability at both room and elevated temperatures was investigated. At room temperature, a maximum of 32.7%, 41.8% and 47.5% removal was achieved by the small, medium and large microgel-based aggregates after 4 methanol extractions. The original uptake efficiency was 39.6%, 44.2% and 52.1%. At elevated temperatures, the uptake efficiency of small, medium and large microgel-based aggregates was 60.2%, 63.4% and 77.6% respectively, compared to the original removal efficiency of 63.1%, 68.1% and 84.6%. These results indicate that the microgels and microgel-based aggregates are not only effective for water remediation,

but show further promise by being easily recycled and reused, without a loss in extraction functionality.

Supporting Information Available: Calibration plot used for the calculation of removal efficiencies for reusability studies.

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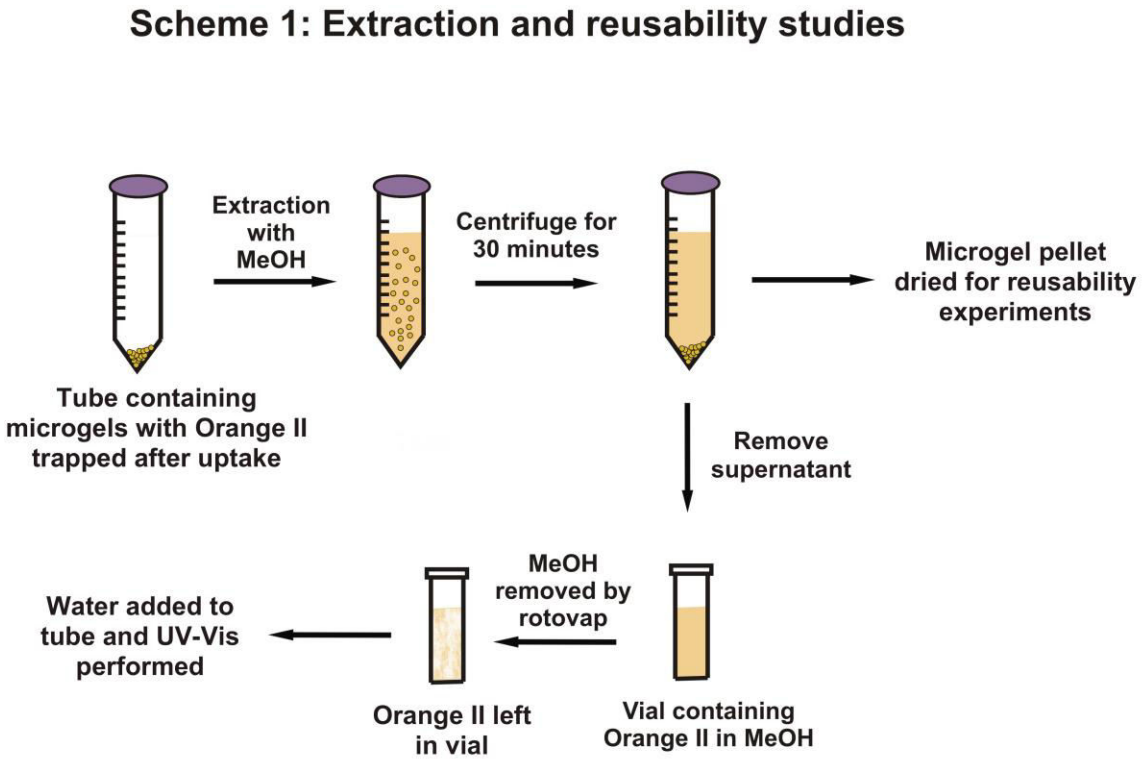
References

1. Theron, J.; Walker, J. A.; Cloete, T. E., *Critical Reviews in Microbiology* **2008,** 34(1) 43-69.
2. Fu, F.; Wang, Q., *Journal of Environmental Management* **2011,** 92(3), 407-418.
3. Lee, M.; Paik, I. S.; Kim, I.; Kang, H.; Lee, S., *J. Hazard. Mater.* **2007,** 144(1-2), 208-214.
4. Erdem, E.; Karapinar, N.; Donat, R., *J. Colloid. Interf. Sci.* **2004,** 280(2), 309-314.
5. Babel, S.; Kurniawan, T. A., *J. Hazard. Mater.* **2003,** *97*(1-3), 219-243.
6. Mohan, D.; Pittman, C. U., *J. Hazard. Mater* **2007,** *142(1-2)*, 1-53.
7. Matilainen, A.; Vepsalainen, M.; Sillanpaa, M., *Adv. Colloid Interfac. Sci.* **2010,** *159(2)*, 189-197
8. Cai, Z. X.; Kim, J. S.; Benjamin, M. M., *Environ. Sci. Technol.* **2008,** *42(2)*, 619-623.
9. Berube, D.; Dorea, C. C., *Wa. Sci. Technol.* **2008,** *8* (5), 505-511.
10. Homem, V.; Santos, L., *J.Environ. Manage.* **2011,** *92* (10), 2304-2347.
11. Pera-Titus, M.; Garcia-Molina, V.; Banos, M. A.; Gimenez, J.; Esplugas, S., *Appl. Catal B-Environ.* **2004,** *47*(4) 219-256.
12. Mohan, D.; Pittman, C. U., *J. Hazard. Mater.* **2006,** *137*(2),762-811.
13. Jusoh, A.; Shiung, L. S.; Ali, N.; Noor, M., *Desalination* **2007,** *206(*1-3), 9-16.
14. Kurniawan, T. A.; Chan, G. Y. S.; Lo, W. H.; Babel, S., *Chem. Eng. J.* **2006,** *118* (1-2), 83-98.
15. Leyva Ramos, R.; Bernal Jacome, L. A.; Mendoza Barron, J.; Fuentes Rubio, L.; Guerrero Coronado, R. M., *J. Hazard. Mater.* **2002,** *90(*1), 27-38.
16. Méndez-Díaz, J. D.; Prados-Joya, G.; Rivera-Utrilla, J.; Leyva-Ramos, R.; Sánchez-Polo, M.; Ferro-García, M. A.; Medellín-Castillo, N. A., *J.Colloid Interfac. Sci.* **2010,** *345(2)*, 481-490.
17. Kim, S. H.; Shon, H. K.; Ngo, H. H., *J. Ind. Eng. Chem.* **2010,** *16*(3) 344-349.

18. Putra, E. K.; Pranowo, R.; Sunarso, J.; Indraswati, N.; Ismadji, S., *Water Res.* **2009,** *43(9)*, 2419-2430.
19. Long, R. Q.; Yang, R. T., *J. Am. Chem. Soc.* **2001,** *123*(9) 2058-2059.
20. Zhou, Q.; Xiao, J.; Wang, W.; Liu, G.; Shi, Q.; Wang, J., *Talanta* **2006,** *68*(4), 1309-1315.
21. Zhou, Q.; Xiao, J.; Wang, W., *J. Chromatogr. A*. **2006,** *1125(*2), 152-158.
22. Zhang, W. X.; Wang, C. B.; Lien, H. L., *Catal. Today* **1998,** *40(4)*, 387-395.
23. Zhang, Z.; Wang, C. C.; Zakaria, R.; Ying, J. Y., *J. Phys. Chem. B* **1998,** *102(*52), 10871-10878.
24. Wang, C. B.; Zhang, W. X., *Environ. Sci. Technol.* **1997,** *31*(7) 2154-2156.
25. Thivaios, I.; Bokias, G., *Journal of Applied Polymer Science* **2010,** *116* (3), 1509-1514.
26. Morris, G. E.; Vincent, B.; Snowden, M. J., *Journal of Colloid and Interface Science* **1997,** *190* (1), 198-205.
27. Wu, Q. L.; Tian, P., *Journal of Applied Polymer Science* **2008,** *109* (6), 3470-3476.
28. Ozkahraman, B.; Acar, I.; Emik, S., *Polymer Bulletin* **2011,** *66* (4), 551-570.
29. Snowden, M.J.; Thomas, D.; Vincent, B. *Analyst*. **1993**, 118, 1367-1369.
30. Schild, H. G., *Progress in Polymer Science* **1992,** *17* (2), 163-249.
31. Wu, C., *Polymer* **1998,** *39* (19), 4609-4619.
32. Wu, C.; Zhou, S. Q., *Macromolecules* **1996,** *29* (5), 1574-1578.
33. Matsuo, E. S.; Tanaka, T., *Journal of Chemical Physics* **1988,** *89* (3), 1695-1703.
34. Serpe, M. J.; Jones, C. D.; Lyon, L. A., *Langmuir* **2003,** *19* (21), 8759-8764.
35. Gong, X. J.; Wu, C.; Ngai, T., *Colloid and Polymer Science* **2010,** *288* (10-11), 1167-1172.
36. Hu, T. J.; You, Y. Z.; Pan, C. Y.; Wu, C., *Journal of Physical Chemistry B* **2002,** *106* (26), 6659-6662.
37. Jones, C. D.; Lyon, L. A., *Macromolecules* **2000,** *33* (22), 8301-8306.
38. Pelton, R., *Adv. Colloid Interfac. Sci.* **2000,** *85* (1), 1-33.
39. Saunders, B. R.; Vincent, B., *Advances in Colloid and Interface Science* **1999,** *80* (1), 1-25.
40. Lyon, L. A.; Debord, J. D.; Debord, S. B.; Jones, C. D.; McGrath, J. G.; Serpe, M. J., *Journal of Physical Chemistry B* **2004,** *108* (50), 19099-19108.
41. 52. Murray, M. J.; Snowden, M. J., *Advances in Colloid and Interface Science* **1995,** *54*, 73-91.
42. Suzuki, D.; McGrath, J. G.; Kawaguchi, H.; Lyon, L. A., *Journal of Physical Chemistry C* **2007,** *111* (15), 5667-5672.
43. Hoare, T.; Pelton, R., *Langmuir* **2004,** *20* (6), 2123-2133.
44. Brugger, B.; Richtering, W., *Langmuir* **2008,** *24* (15), 7769-7777.
45. Nayak, S.; Debord, S. B.; Lyon, L. A., *Langmuir* **2003,** *19* (18), 7374-7379.
46. 34. Lutz, J. F.; Weichenhan, K.; Akdemir, O.; Hoth, A., *Macromolecules* **2007,** *40* (7), 2503-2508.
47. Dupin, D.; Fujii, S.; Armes, S. P.; Reeve, P.; Baxter, S. M., *Langmuir* **2006,** *22* (7), 3381-3387.
48. Amalvy, J. I.; Wanless, E. J.; Li, Y.; Michailidou, V.; Armes, S. P.; Duccini, Y., *Langmuir* **2004,** *20* (21), 8992-8999.

49. Plunkett, K. N.; Kraft, M. L.; Yu, Q.; Moore, J. S., *Macromolecules* **2003,** *36* (11), 3960-3966.
50. Serpe, M. J.; Rivera, M.; Kersey, F. R.; Clark, R. L.; Craig, S. L., *Langmuir* **2008,** *24* (9), 4738-4742.
51. Nayak, S.; Lyon, L. A., *Chemistry of Materials* **2004,** *16* (13), 2623-2627.
52. Miyata, T.; Asami, N.; Uragami, T., *Nature* **1999,** *399* (6738), 766-769

53. Snowden, M. J.; Chowdhry, B. Z.; Vincent, B.; Morris, G. E., *Journal of the Chemical Society-Faraday Transactions* **1996,** *92* (24), 5013-5016.
54. Schmidt, S.; Hellweg, T.; von Klitzing, R., *Langmuir* **2008,** *24* (21), 12595-12602.
55. Kratz, K.; Hellweg, T.; Eimer, W., *Colloids and Surfaces a-Physicochemical and Engineering Aspects* **2000,** *170* (2-3), 137-149.
56. Sorrell, C. D.; Carter, M. C. D.; Serpe, M. J., *Advanced Functional Materials* **2011,** *21* (3), 425-433.
57. Parasuraman, D.; Serpe, M. J., *ACS Applied Materials & Interfaces* **2011**, *3*(7) 2732-2737.
58. Parasuraman, D.; Serpe, M. J., *ACS Applied Materials & Interfaces* **2011**, 3(12), 4714-4721.
59. Parasuraman, D.; Leung, E.; Serpe, M. J., *Colloid Polym. Sci.* **2012**, 290(11), 1053-1067.
60. Parasuraman, D.; Sarker, A.K.; Serpe, M.J.; *ChemPhysChem.* **2012**, 13(10), 2507-2515.
61. Meng, Z.Y.; Smith, M.H.; Lyon, L.A., Colloid Polym. Sci. 2009, 287 (3), 277-285.



Scheme 1. Schematic depicting the extraction process used in this study.

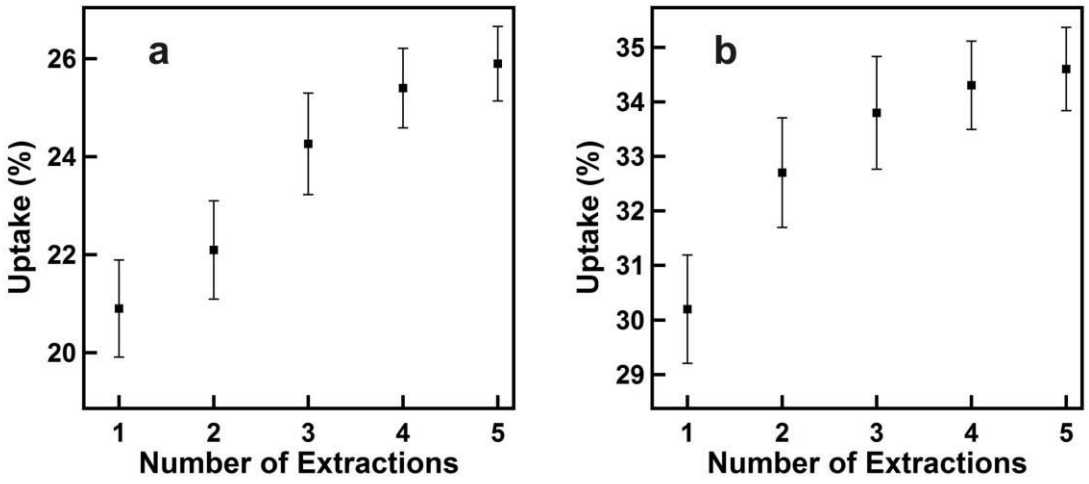


Figure 1. Trend of percent uptake of Orange II as a function of the number of MeOH extraction cycles for (a) pNIPAm-co-AAc-2 and (b) pNIPAm-co-AAc-3 microgels at room temperature. Each point on the plot represents an average of three replicate experiments of uptake studies and the error bars denote the standard deviation.

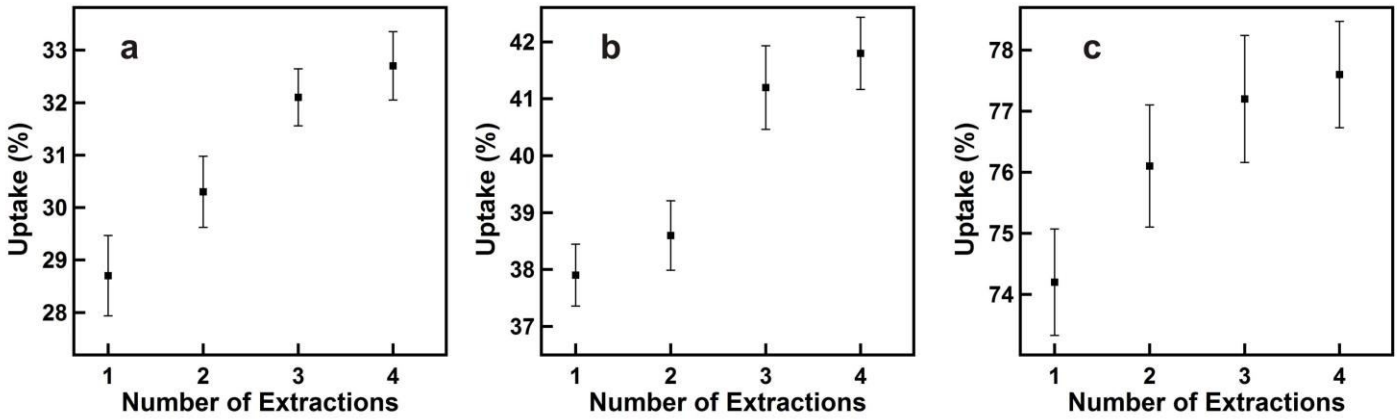


Figure 2. Trend of percent uptake of Orange II as a function of the number of MeOH extraction cycles for (a) pNIPAm-*co*-AAc-1 microgel-based aggregates, (b) pNIPAm-*co*-AAc-2 microgel-based aggregates and (c) pNIPAm-*co*-AAc-3 microgel-based aggregates, at room temperature. Each point on the plot represents an average of three replicate uptake experiments after the given number of extractions and the error bars denote the standard deviation.

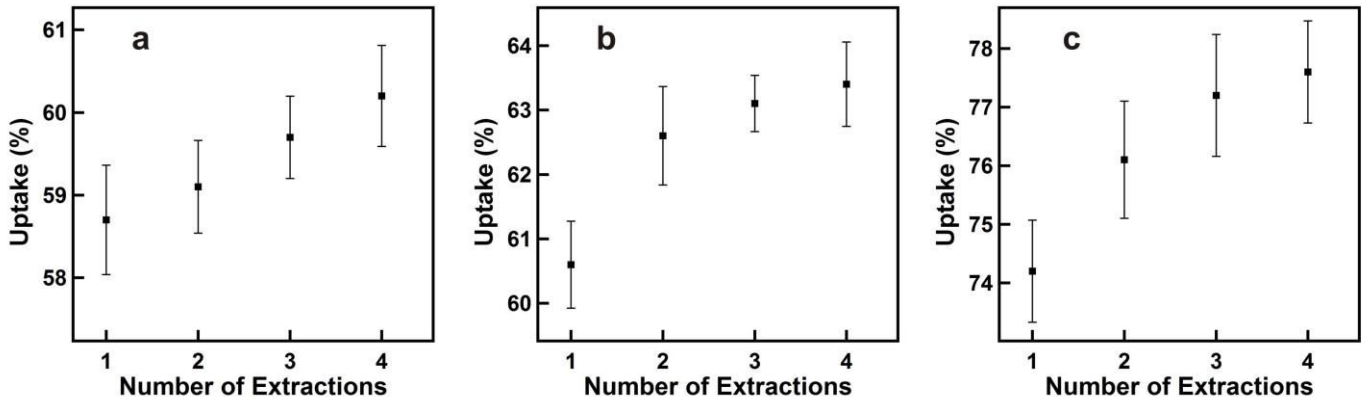


Figure 3. Trend of percent uptake of Orange II as a function of the number of MeOH extraction cycles for (a) pNIPAm-*co*-AAc-1 microgel-based aggregates, (b) pNIPAm-*co*-AAc-2 microgel-based aggregates and (c) pNIPAm-*co*-AAc-3 microgel-based aggregates at elevated temperature. Each point on the plot represents an average of three replicate uptake experiments after the given number of extractions and the error bars denote the standard deviation.

Supporting Information

Recyclability of Poly (*N*-Isopropylacrylamide) Microgel Based Assemblies for Organic Dye Removal from Water

*Deepika Parasuraman, Avijeet K. Sarker and Michael J. Serpe**

Department of Chemistry, University of Alberta, Edmonton, AB, T6G 2G2

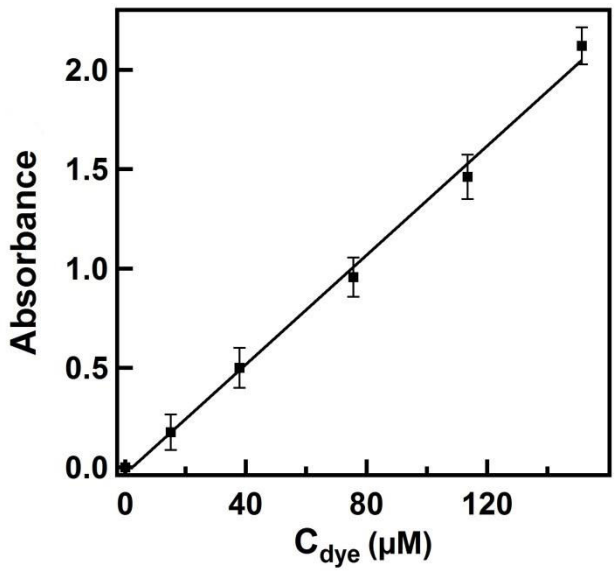


Figure SI1. Calibration curve for Orange II. Each point on the plot represents an average of three replicate experiments and the error bars denote the standard deviation. The correlation coefficient, R^2 value was analyzed to be 0.9951. The equation of the line to calculate the concentrations of Orange II was y= 0.0138*x-0.0327.