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Poly(ethylene glycol) (PEG)-based microgels embedded with magnetic nanoparticles for tannin removal and valorization

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Abstract−Excess tannin in drinks can lead to unpleasant astringent taste, pinking or browning, as well as a decrease in clarity. While protein precipitation method in which various proteins and synthetic polymers are added to induce tannin-protein complexation, followed by separation *via* sedimentation, is widely used for tannin removal, sedimentation time can take up to few days. In this work, we present poly(ethylene glycol) (PEG)-based microgels embedded with magnetic nanoparticles (MNP) as fining agents for effective adsorption and removal of tannins, using tannic acid (TA) as the model tannin. The PEG microgel with high surface area enables the tannins to effectively adsorb through hydrogen-bonding, and the incorporated MNP enables facile recovery of TA adsorbed microgel *via* magnetic decantation. We also demonstrate that the PEG microgel is reusable and the TA adsorbed can be also valorized into ellagic acid (EA) by simple base treatment of the TA adsorbed microgels.

Keywords: Tannins, Microgels, Poly(ethylene glycol), Removal, Valorization

INTRODUCTION

Tannins are a class of polyphenolic compounds with a bitter and astringent taste that is naturally present in the bark of many trees and leaves [1]. They are also abundant in fruits including grape, chokeberry, and blueberry, as well as drinks made from these such as grape juices and wines. Tannin removal is an important quality-control factor in the manufacturing of tannin-rich drinks [2], as excess tannin can lead to unpleasant astringent taste, pinking or browning by additional oxidation, and a decrease in clarity due to the precipitates formed by the small of amount of plant proteins present in these drinks [3,4]. While tannins largely vary in physicochemical properties, including size and molecular weight, they are generally known to bind with proteins through hydrogen-bonding and precipitate due to formation of water-insoluble tannin-protein complexes. As a result, the most common approach to remove tannins from drinks is protein precipitation in which proteins are additionally introduced to induce tannin-protein complexation, followed by separation *via* sedimentation.

A wide variety of water-soluble proteins have been utilized for such protein precipitation-based tannin removal. While animal-derived proteins, such as egg albumin, gelatin, and caseinates, traditionally have been used for this purpose [5,6], plant-derived proteins, such as wheat gluten [7,8], potato patatin [8,9], pea protein [10,11], as well as synthetic polymers including poly(ethylene glycol) (PEG) and polyvinylpyrrolidone (PVP), have been recently used to minimize allergic responses [12]. However, the time required for the resulting tannin-protein or tannin-polymer complexes to settle can take up to few days due to the extremely small-sized precipitates [13,14]. Ultracentrifugation can accelerate the sedimentation process, but the excess protein used as well as the resulting ultra-fine precipitates may still remain in the solution, raising allergy issues [15].

Alternatively, solid particles that can bind with tannins through hydrogen-bonding have been employed as fining agents to mitigate the long sedimentation time. Polyvinylpolypyrrolidone (PVPP) powder, a highly crosslinked modification of PVP [13,16,17] as well as micro-sized hydrogel particles, or microgels, consisting of polymers that can hydrogen-bond with tannins have been used as fining agents. For instance, Cao et al. demonstrated that polyacrylamide microgels with tunable particle size allow effective removal of tannins and fine control over the sedimentation velocity [18]. Another advantage of using solid particles as fining agents is their reusability with proper post-processing [19,20], which increases their economic efficacy while reducing the environmental impact. However, complete precipitation still takes time on the order of several hours even with these fining agents [13]. While filtration and centrifugation have been additionally employed along with fining agents to facilitate the separation process, these methods either yield membrane fouling [21,22] or require high installation cost, limiting their broader applicability. More importantly, while the fining agent, as well as the adsorbed tannins, can be retrieved during the recycling process, this potential has not been explored thoroughly. Therefore, there is an unmet need for a facile and non-contact-based method in the separation of fining agents for effective removal of tannins as well as retrieval of the adsorbed tannins from these fining agents in a valuable form.

In this study, we utilized droplet microfluidics to prepare PEG-based microgels embedded with magnetic nanoparticles (MNP) for effective adsorption and removal of tannic acid (TA), one of the representative tannins, from ideal solutions as well as tannins in an

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actual grape juice. The PEG moieties within the microgel effectively bind with the tannins *via* hydrogen-bonding. Additional incorporation of MNP into the PEG microgel enables facile recovery of TA adsorbed microgel *via* magnetic decantation. We also demonstrate that the PEG microgel is reusable and the TA adsorbed can be also valorized into ellagic acid (EA), one of the promising next-generation biomaterials with antioxidant property that are known to assist cellular homeostasis [23], by simple base treatment of the TA adsorbed microgels.

MATERIALS AND METHODS

1. Materials

Polyethylene glycol diacrylate (PEGDA, M_n=700), Span® 80 (nonionic surfactant, sorbitan monooleate), mineral oil (light), 2-hydroxy-4′-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacure® 2959, photoinitiator, 98%), magnetic iron (II, III) oxide (Fe_3O_4) nanoparticles (MNP) with an average diameter of 100 nm, Folin-Ciocalteu's phenol reagent (suitable for determination of total protein by Lowry method, 2 N), sodium bicarbonate (≥99.7%), tannic acid (TA), poly(vinylpolypyrrolidone) (PVPP, ~110 μm particle size) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Ellagic acid dihydrate (M_w=338.22, >98.0%) was purchased from Tokyo Chemical Industry (Tokyo, Japan). Sodium carbonate anhydrous (>99.5%), and 2-propanol (>99.8%) were purchased from Samchun Pure Chemical (Pyeongtaek, Korea). Commercial grape juice (Lotte Chilsung Beverage) was purchased from a GS25 convenience store and was used for validation of the tannin removal efficacy. High-performance liquid chromatography (HPLC) analysis for the validation and quantification of synthesized EA was performed using a Shimadzu Prominence UFLC^{TM} system with a UV detector and ZORBAX eclipse XDB-C18 analytical column (4.6×150 mm, 5 μm). All chemicals used in HPLC analysis were HPLC-grade reagents.

2. Fabrication of Poly(ethylene glycol) (PEG) Microgels

PEG microgels were fabricated by *in-situ* photopolymerization of water-in-oil (W/O) emulsion droplets containing poly(ethylene glycol) diacrylate (PEGDA) (M_n=700) as the monomer. Specifically, 1% (w/w) Fe_3O_4 nanoparticle suspension in distilled water, or MNP solution, was first prepared by vigorous vortexing and sonicating overnight. Then, 30% (w/w) PEGDA aqueous solution containing 3% (w/w) Irgacure® 2959 (photoinitiator) was separately prepared. By mixing PEGDA solution, MNP solution, and distilled water in 2 : 1 : 1 volume ratio, the precursor mixture was prepared. The final concentration of PEGDA in the precursor mixture was 15% and was sonicated shortly prior to use.

W/O emulsion droplets with the precursor mixture as the dispersed phase were produced using a glass capillary microfluidic device with a counter-flow configuration as described previously [1]. For the continuous phase, mineral oil with 2% (w/w) span® 80 was used. The emulsion droplets were exposed to UV light (320-500 nm) for *in situ* photopolymerization. The polymerized droplets were collected in a glass vial containing a small amount of continuous phase. The resulting microgels were washed with isopropyl alcohol several times to remove the unreacted monomer as well as the oil prior to transfer to distilled water for storage. The flow rates during microgel formation were set as 1,000 μl/h for the inner phase and 15,000 μl/h for the continuous phase. The analogous larger microgels were fabricated using the same procedure except for the continuous phase flow rate which was set at 4,000 μl/h.

3. Evaluation of Tannin Removal with PEG Microgels

Tannic acid (TA) was used as the model for tannins in drinks. Predetermined amount of hydrated PEG microgels embedded with MNP was transferred to a 10 ml glass vial, with minimal water. Then, 10 ml of either grape juice or TA solution with known concentration was added into the vial. Both solutions were freshly prepared and shaded from light during all experimental processes. Prior to measurement, the vials were shaken using a shaker plate at 100 rpm for 240 min. The amount of tannins adsorbed by the PEG microgels was quantified by measuring the remaining TA amount in the solution after adsorption. The TA amount in the solution was determined by following the Folin-Ciocalteu method in which a colorimetric assay is used to measure the phenolic compounds [24]. To quantify the TA amount in each sample, calibration curve was first acquired using 5 μg, 15 μg, 25 μg, 35 μg, and 50 μg of TA. In the case of grape juice, the remaining tannin amount in the vial after PEG microgel removal was calculated by ruling out the non-tannin phenolic compound from the total phenolic compound [24]. After PEG microgels adsorbed tannins, the tannins were removed from the microgels by NaOH treatment for valorization and reuse of the microgels; the base treatment leads to the weakening of the hydrogen bonding of tannins with the PEG microgels [12]. The tannins adsorbed on the PEG microgels were washed several times with 0.1 M NaOH solution until the color of the solution did not change. Then, they were subsequently washed with distilled water.

4. EA Synthesis from Tannins and Characterization Using HPLC

The TA adsorbed on PEG microgels (embedded with MNP) were converted to EA, following the protocol similar to that proposed by Mizusawa et al. [25]. Briefly, 0.12 g of PEG microgels was dispersed in 10 ml of 1 mg/ml TA solution for 240 min to capture TA. This led to adsorption of approximately 8.9 mg of TA on microgels. The microgels were separated by magnetic decantation and washed three times with distilled water. Then, 5 ml of distilled water and 40 μl of NaOH 40% (w/w) solution were added and vortexed for 15 s. Next, 0.315 g of $NaHCO_3$ powder was added, followed by shaking using a rotary shaker. After 24 h, 1 ml of HCl (0.1 M) was added as a terminal step. The resulting solution was separated from PEG microgels with magnetic decantation and then centrifuged. The precipitate was dried at room temperature for subsequent HPLC analysis. The dried precipitate was dissolved in dimethyl sulfoxide (DMSO) to make 1 mg/ml solution. Then, a solvent mixture composed of acetonitrile : distilled water=1 : 1 was used to further dilute to 100 μg/ml solution. In HPLC analysis, formic acid 1% aqueous solution was used for the mobile phase A, while acetonitrile was used as the mobile phase B. Solvent gradient condition was used from that of Kim et al. [23]. A chromatogram was detected at 254 nm and the injection volume was 20 μl. To acquire the calibration curve, EA standard was dissolved in dimethyl sulfoxide to make a 100 μg/ml EA stock solution. With a solvent that is composed of acetonitrile : distilled water=1 : 1, 20 μg/ml, 40 μg/ml, 60 μg/ml, 80 μg/ml, and 100 μg/ml EA solution was prepared by subsequently

diluting the stock solution. A calibration curve was drawn from the peak area of the chromatogram from each concentration of EA standard solution. Synthesized EA sample was quantified using the acquired calibration curve.

RESULTS AND DISCUSSION

1. Design of Highly Efficient Fining Agents for Removal and Valorization of Tannins

For highly efficient removal of tannins and subsequent valorization, the fining agent needs to preferably interact with tannins while suppressing non-specific adsorption of proteins or any other substances in the media. In addition, the fining agent requires exhibiting high surface area for effective adsorption of tannins while providing the means to facilitate the separation process for subsequent retrieval of the fining agent for reuse and the adsorbed tannin for valorization. To fulfill all these sophisticated demands, biocompatible microgels consisting of materials such as PEG that can hydrogen-bond with tannin while exhibiting anti-fouling property need to be prepared [12,26,27]. Moreover, for facile recovery of the fining agent *via* magnetic decantation after adsorption and removal from the tannin-containing solution, MNP larger than the mesh size of the hydrogel matrix needs to be incorporated into the PEG microgel, as schematically illustrated in Fig. 1. This allows subsequent release and transformation of the adsorbed TA into a valuable form as well as effective recovery of the PEG microgel for reuse by simple base treatment of the TA adsorbed PEG microgels.

2. Fabrication of Poly(ethylene glycol) (PEG) Microgels Using Droplet Microfluidics

To prepare these MNP-embedded PEG microgels in a simple and robust manner, we employed droplet microfluidics in which a glass capillary microfluidic device is used to prepare monodisperse W/O emulsion droplets consisting of a photocurable PEG monomer, PEGDA, as shown in Fig. 2(a). An aqueous solution containing PEGDA, photoinitiator, and MNP is injected as the dispersed phase while the continuous mineral oil phase containing surfactant is introduced from the opposite direction to emulsify the dispersed phase by shearing, forming highly uniform W/O emulsion droplets. The stream of emulsion droplets produced are *in situ* polymerized at the end of the device upon UV exposure, yielding PEG microgels embedded with MNP (Fig. 2(b)). The resulting PEG microgels exhibit a mean diameter of 127 μm and are monodisperse, as shown by the low value of coefficient of variation (CV=3.61%) and their distribution (Fig. 2(c)). To remove the unreacted PEGDA within the PEG microgel that can potentially hydrogen-bond with tannin and lead to precipitate formation, we thoroughly washed the microgels several times with isopropyl alcohol and distilled water. The rinsed microgels effectively retained the incorporated MNP within the hydrogel matrix, as evidenced by the strong attraction of the microgel upon introducing a permanent magnet near the PEG microgel suspension as shown in Fig. 2(d) and Supporting Information Fig. S1. This clearly demonstrates the potential of these microgels in facile separation and retrieval for reuse and valorization *via* magnetic decantation.

3. Evaluation of Tannin Removal Performance

To determine the tannin removal performance of these MNP-embedded PEG microgels, we first prepared two sets of microgels with the same composition but with different sizes, in which one is the microgels presented in Fig. 2(b) with a mean diameter of 127 μm (defined as small microgels), while the other is separately pre-

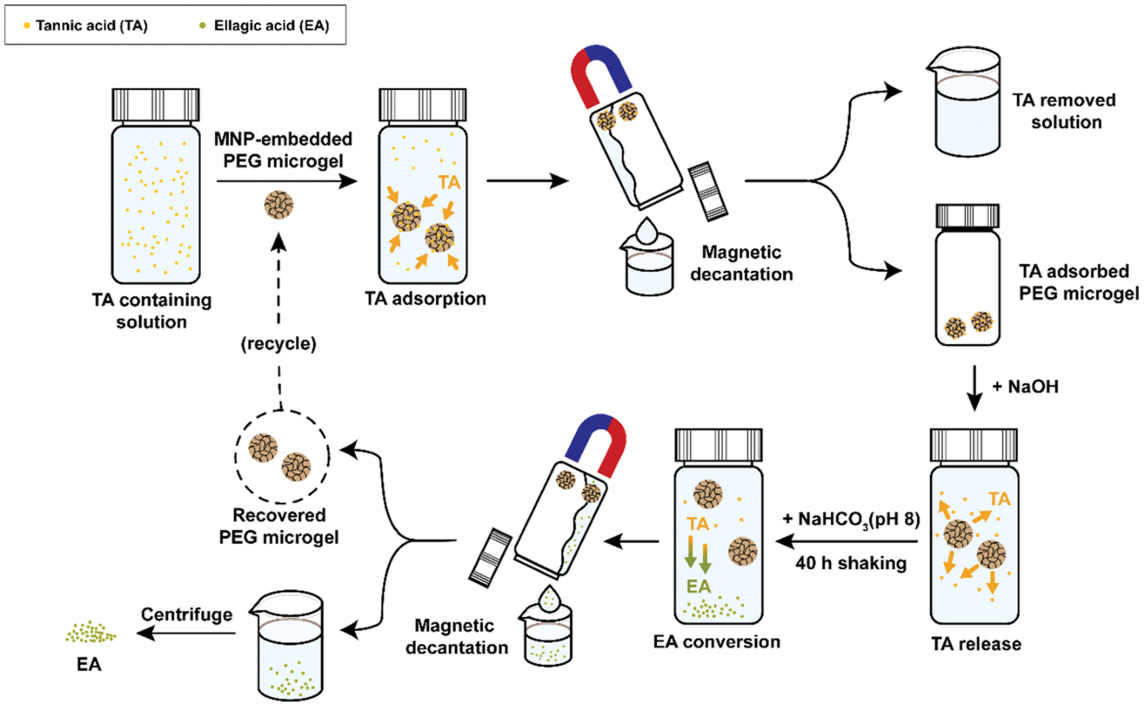

Fig. 1. Schematic illustrating the overall process of tannin removal and valorization using magnetic nanoparticle (MNP)-embedded poly(ethylene glycol) (PEG) microgels.

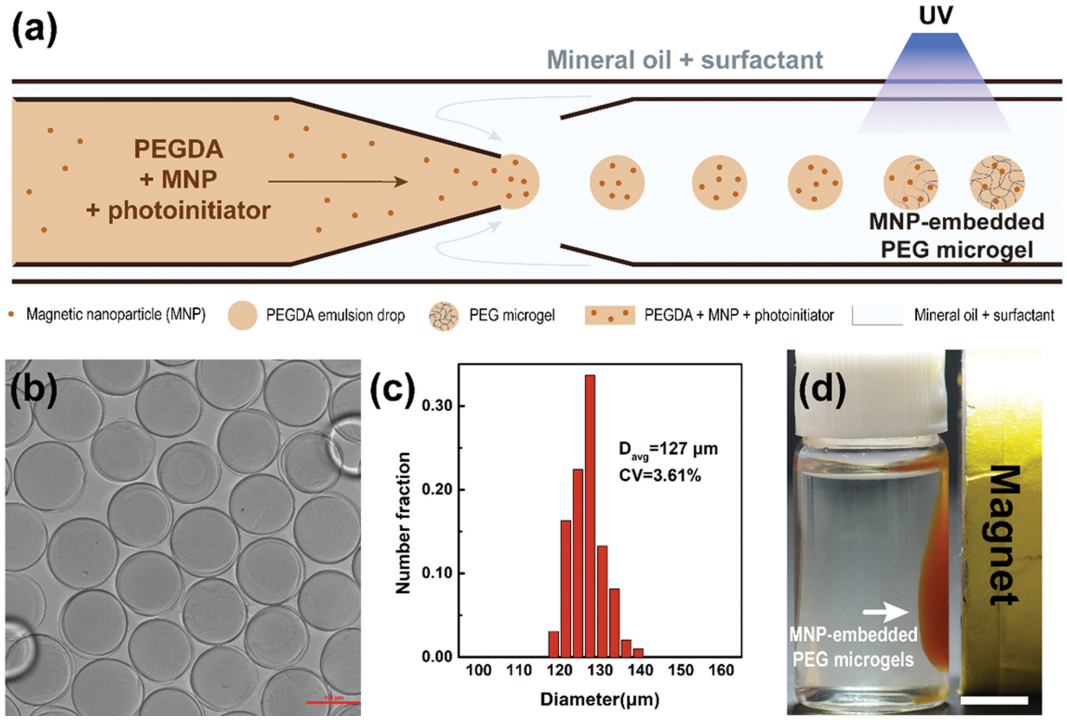

Fig. 2. (a) Schematics of the glass capillary based microfluidic device used to prepare magnetic nanoparticle (MNP)-embedded poly(ethylene glycol) (PEG) microgels. (b) Optical micrograph showing the produced MNP-embedded PEG microgels. The scale bar represents 100 μm. (c) A histogram showing the size distribution of the PEG microgels. The average diameter and CV value are presented within the plot. (d) A photograph showing the magnetic response of the MNP-embedded PEG microgels dispersed in aqueous media. The scale bar represents 10 mm.

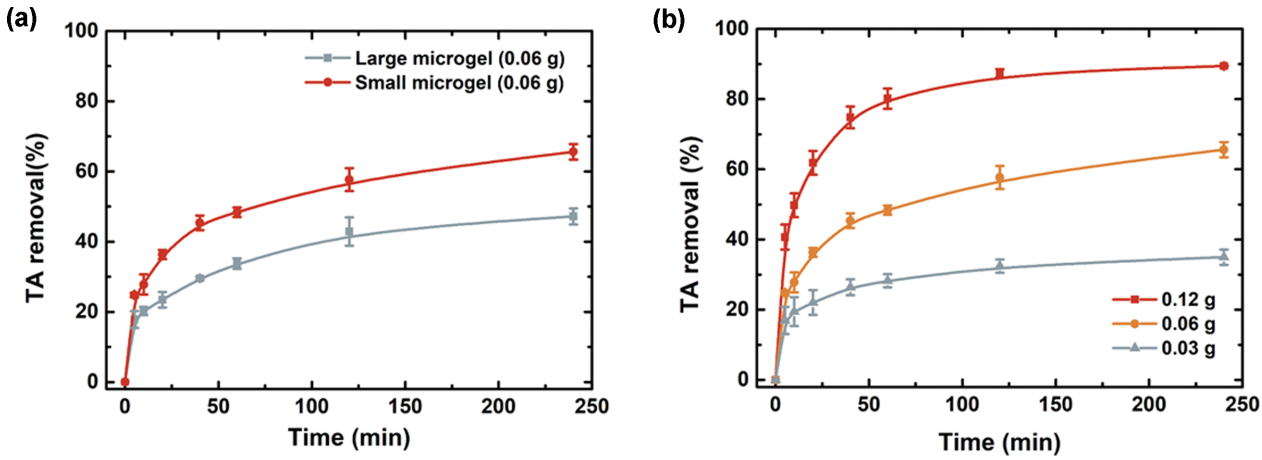

Fig. 3. (a) Tannic acid (TA) removal plot on poly(ethylene glycol) (PEG) microgels with different sizes. The same amount (0.06 g) of microgels were used and the mean diameters of the small and large microgels were 127 and 334 μm, respectively. (b) A TA removal plot with different amounts of PEG microgels. All experiments were repeated three times.

pared larger ones with a mean diameter of 334 μm (CV=2.7%). We note that the 127 μm PEG microgel is the smallest microgel that can be reliably and uniformly produced using this glass capillary microfluidic device in dripping regime. The larger PEG microgels (denoted as large microgels) were prepared by decreasing the continuous phase flow rate while keeping the dispersed phase constant during emulsion production. Then, we measured the extent of tannin removal (%) by using TA solution with known concentration as the model tannin solution. Monitoring the extent of TA removal with time after addition of the same amount (0.06 g) of PEG microgels with different sizes into two separate vials containing 10 ml of 1 mg/ml TA solutions showed that the small microgels exhibit faster adsorption rate as well as larger adsorption capacity than the larger microgels due to larger specific surface area (Fig. 3(a)). Thus, for simplicity, we denote small microgels with a mean diameter of 127 μm as PEG microgels hereafter. Also, the dose-

dependent removal of TA was evaluated by monitoring the extent of TA removal upon addition of different amounts of PEG microgels, 0.03, 0.06, and 0.12 g, respectively, into separate vials containing the same amount and concentration of TA solution (10 ml, 1 mg/ml). As expected, we observed that the adsorption rate and the capacity scales with the microgel amount and the extent of TA removal can reach up to 89% when 0.12 g of PEG microgels are added, as shown in the plot of Fig. 3(b).

4. Valorization: Ellagic Acid (EA) Conversion from Tannic Acid

As one of the key advantages of fining agents is their reusability, we also examined whether the adsorbed tannins can be retrieved during the recycling process. We note that TA adsorbs onto the PEG microgel *via* hydrogen bonding, and thus increasing the pH above the pKa of TA weakens the interaction to dissociate TA from the PEG microgel [12]. However, at the same time, increasing the pH also facilitates the hydrolysis of TA. As a result, instead of retrieving TA itself, we directly converted it to EA, a biomolecule which has antioxidant effect and helps cellular homeostasis. In particular, the adsorbed tannins are first hydrolyzed to form gallic acid (GA), followed by dimerization, yielding EA as shown in Fig. 4(a) [25]. To achieve this, we synthesized EA by first adding NaOH and vortexing to dissociate TA from the PEG microgels. Then, Na_2CO_3 was added as a buffer (pH 8.6) and incubated for 40 h, leading to formation of EA which appears as a dark olive colored precipitate due to its hydrophobicity. High performance liquid chromatography was also performed to verify that the synthesized material is EA. Comparing the HPLC chromatogram of the EA synthesized from the TA adsorbed PEG microgel with the standard EA solution revealed that they both exhibit a distinct peak around 22 min with no other peaks as shown in Fig. 4(b). We note that a weak peak that appears near 4 min is attributed to the DMSO used as the solvent. Moreover, a calibration curve was derived from the EA standard solution to acquire the conversion yield of 16.2% (w/w), which was calculated by dividing the weight of the synthesized EA by the weight of the TA captured on the microgel. To verify the origin of this low conversion yield, we performed a separate experiment in which we directly synthesized EA from TA powder (8.9 mg), which was equivalent to the amount captured on the PEG microgel and separately evaluated the conversion yield to determine the valorization efficiency of free TA in solution. This yield, 15.8% (w/w), was almost identical to the value acquired from TA adsorbed on PEG microgel, indicating that it is not the nature of TA whether they are adsorbed on the microgel or exist freely in solution that leads to low conversion yield. Instead, we believe that a large portion of TA was transformed into other compounds, such as quinone and semiquinone, which are generated by oxidative side reactions [28] or discarded during the HPLC sample preparation process.

5. Reusability and Applicability to Commercial Grape Juice

To investigate whether the PEG microgels can be reused after the base treatment, which weakens PEG-TA hydrogen bonding and induces base-catalyzed hydrolysis of TA, we measured the change in the extent of tannin removal for PEG microgel with respect to each adsorption/base treatment cycle as shown in Fig. 5(a). We noted that the microgels were additionally treated with basic solution (0.1 M NaOH) to completely remove the adsorbed TA from the microgels. We observed approximately 60-70% TA removal in the first cycle when 0.06 g of PEG microgels was applied to 1 mg/ml TA solution, similar to the results shown in Fig. 3(a). Also, PEG microgels exhibit a moderate decrease in adsorption capacity with only 3% performance deterioration in average after each cycle, demonstrating their excellent reusability.

To further extend the utility of these PEG microgels in the removal of tannins from commercial grape juice, we first measured the total tannin concentration in grape juice, which is equivalent to 0.72 mg/ml TA solution. Then, we added 0.12 g of PEG microgels to both grape juice and 0.72 mg/ml TA solution and monitored the extent of removal with time as shown in Fig. 5(b). We found that 94.2% of tannins were removed from 0.72 mg/ml TA solution, while 60.3% were removed from grape juice. Even when the amount of microgel was doubled to 0.24 g, the final TA adsorption amount increased only by 6.5% to 66.8%. The reduction

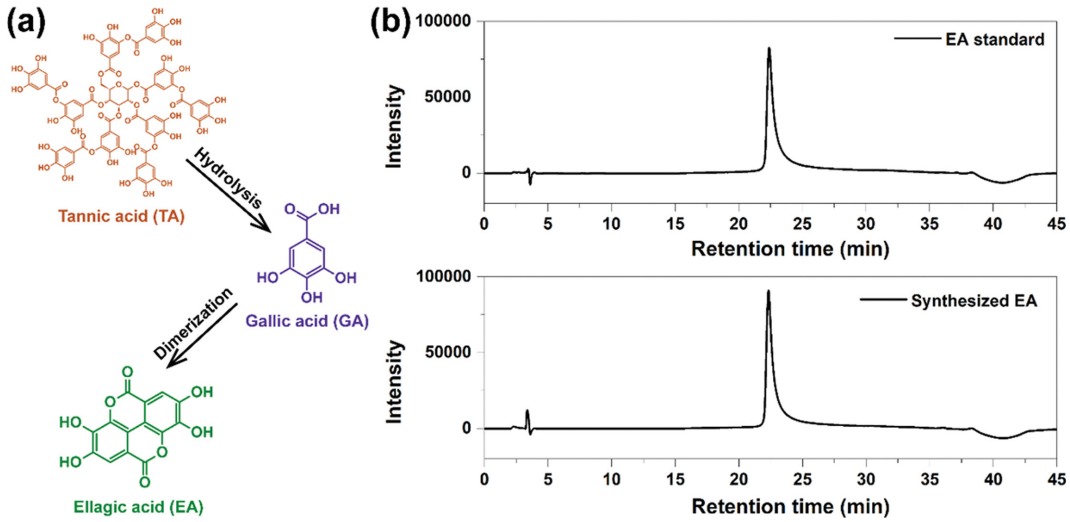

Fig. 4. (a) Schematic illustrating the simplified mechanism of ellagic acid (EA) synthesis from tannic acid (TA). (b) HPLC chromatogram of EA standard solution (20 μg/ml) and synthesized EA from TA-adsorbed poly(ethylene glycol) (PEG) microgels.

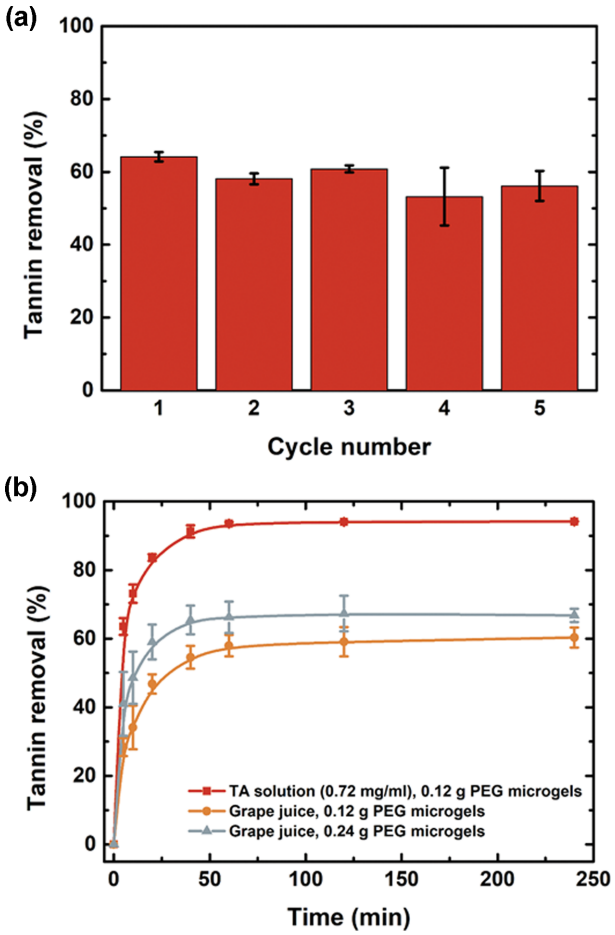

Fig. 5. (a) A plot showing the change in the extent of tannin removal for poly(ethylene glycol) (PEG) microgels with respect to each adsorption/base treatment cycle. (b) Plot showing tannin removal performance of PEG microgels in grape juice. A tannic acid (TA) solution with the equivalent tannin concentration was also tested and shown for comparison. All experiments were repeated three times.

in tannin removal performance for grape juice compared to the model tannin solution consisting solely of TA is possibly due to the presence of other high molecular biomaterials (such as anthocyanins and catechins) besides tannins that can adsorb by hydrogen bonding as well as vegetable proteins that can also bind with tannins, all of which may reduce the tannin adsorption capacity of the PEG microgel.

CONCLUSION

Herein, we present PEG microgels embedded with magnetic nanoparticles as fining agents to remove tannins from tannin-rich drinks. Performing a series of adsorption experiments with variation in size and the amount of microgels revealed that the larger the amount of microgel and the smaller the size, the better the tannin removal performance. In addition, we show that tannins in commercial grape juice can also be removed, while up to 94% of tannins from model tannin solution consisting of TA can be removed through adsorption. Moreover, we demonstrate that not only can the PEG microgel be reused without significant deterioration in adsorption capacity, but also the TA adsorbed on microgels can be readily converted into EA through magnetic decantation and base treatment. We anticipate that the MNP-embedded PEG microgels presented in this work will provide a new, reusable method for the effective removal of tannins and subsequent valorization into EA.

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SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

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Supporting Information

Poly(ethylene glycol) (PEG)-based microgels embedded with magnetic nanoparticles for tannin removal and valorization

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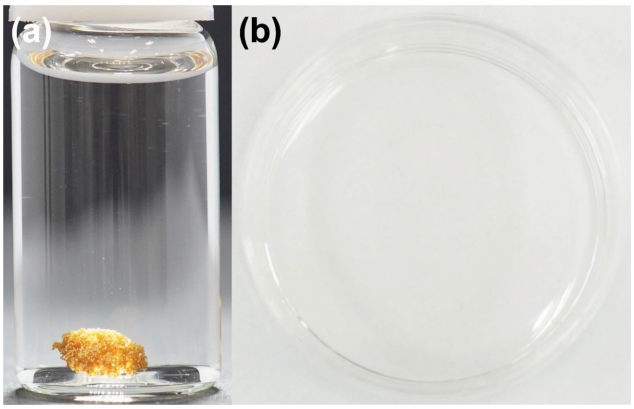

Fig. S1. (a) A photograph of poly(ethylene glycol) (PEG) microgels aggregated into a single mass in tannic acid (TA) solution. The photograph was taken 4 h after putting the microgels into the solution. The PEG microgels aggregate into a single mass after TA adsorption due to the presence of multiple sites in TA that can hydrogen bond with PEG microgels. Also, the agglomerated microgel mass is much easier to magnetically decant than individual particles and they dissociate into individual particles after the base treatment cycle for subsequent reuse. (b) A photograph of the TA solution after removal of the agglomerated microgel mass *via* magnetic decantation. Following magnetic decantation, no other smaller particles remain in the sample.