

Tough Poly(L-DOPA)-containing Double Network Hydrogel Beads with High Capacity of Dye Adsorption

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 Electronic Supplementary Information

Abstract Developing a low-cost and well-recyclable adsorbent with high adsorption capacity is greatly desirable in dye wastewater treatment. Here, we demonstrate a kind of novel tough and reusable hydrogel beads with quite high capacity of dye adsorption *via* incorporating mussel-bioinspired poly(L-DOPA) (PDOPA) into alginate/poly(acrylamide) double network (DN) hydrogels. The synthesized PDOPA nanoaggregates were introduced into the DN hydrogels by simple one-pot mixing with the monomers prior to polymerization. The fabricated hydrogel beads exhibited high mechanical strength and good elastic recovery due to the interpenetrating Ca^{2+} -alginate and poly(acrylamide) networks. It was shown that the beads exhibited relatively high dye adsorption capacity compared to other adsorbents reported in literature, and the introduction of PDOPA with an appropriate amount raised the adsorption capacity. It is believed that the addition of PDOPA and the matrix of double network architecture contributed synergistically to the high adsorption capacity of hydrogel beads. Moreover, the desorption of dyes could be easily realized *via* rinsing in acidic water and ethanol solution. The hydrogel beads remained the high adsorption capacity even after 5 times of adsorption and desorption cycles. This tough and stable hydrogel with high adsorption capacity may have potential in treatment of dye wastewater released by textile dyeing industry.

Keywords Dye adsorption; Hydrogel beads; Poly(L-DOPA); Double network; High strength

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INTRODUCTION

In recent years, much attention has been paid to the continuously increasing global water pollution^[1]. Discharging wastewater without treatment often causes many environmental and human health problems^[2, 3]. A lot of technologies have been developed to remove the heavy metal, organic dyes and other chemical pollutants from wastewater, including filtration, chemical precipitation, adsorption and photodegradation^[4–8] *etc.* Among these decontamination techniques, adsorption is widely used as a cost-effective method and lots of adsorbents have already been commercialized in wastewater treatment. However, most commercial adsorbents, such as activated carbon, zeolite, metal oxides nanoparticles and polymer-based materials^[9–12], meet some critical issues like difficult regeneration, low efficiency and low adsorption capacities. In recent years, with the development of theoretical research and new techniques, more and more nanomaterials are developed and used as adsorbents in water treatment^[13–16]. Although these new nanomaterials show a promising

potential in water treatment, few concerns have been made on the durability and recovery of adsorbents. It should be taken into consideration that the degradation and incomplete recovery of nanoscale adsorbents might cause a second contamination^[17, 18].

Hydrogels are hydrophilic polymer networks containing large quantities of water without dissolving, which are widely used as biomedical, architectural and environmental materials^[19–21]. It has been proved that hydrogels are effective adsorbents or adsorbent loaders because of the rapid diffusion and entrapment of water-soluble substances in the networks^[18, 22]. Moreover, most hydrogels are free-standing with designable morphologies, which facilitates the removal of hydrogel after adsorption saturation. However, conventional hydrogels always suffer from swelling as the mechanical strength dramatically decreases, which limits the application in adsorption process. In order to obtain a tough hydrogel system, Gong *et al.*^[23, 24] proposed and developed a class of double-network (DN) hydrogels consisting of a highly cross-linked first network and a flexible and soft second polymer network. The DN hydrogels exhibit extraordinary mechanical strength and toughness, and have great potential applications in tissue engineering, drug carriers and other functional materials^[25]. To our knowledge, so far only few DN hydrogels in literature have been

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reported for adsorption process, *e.g.*, graphene oxide (GO) was used as an additive or as the second network for fabricating the tough hydrogel adsorbent^[26–28]. Moreover, most bulk hydrogel samples exhibited poor adsorption performance, because the adsorbed molecules at the surface would affect the consecutive adsorption process^[29, 30]. Therefore, it is highly desirable to develop a tough DN hydrogel adsorbent with high adsorption capacity for the removal of various dyes from wastewater.

Herein we demonstrate the fabrication and application of tough poly(L-DOPA) (PDOPA)-containing DN hydrogel beads with good adsorption ability to dyes. PDOPA is reaction products of the auto-oxidation and self-polymerization of L-3,4-dihydroxyphenylalanine (L-DOPA) in weak alkaline solution. L-DOPA is an important amino acid in mussel foot proteins^[31], which is found to play a crucial role in the strong adhesion of mussel byssus onto solid surface. L-DOPA and its catechol derivatives have been extensively used for material surface modification based on their self-polymerization and strong adhesion behaviors^[5]. The adsorption characteristics of PDOPA have been reported and it is proposed that the catechol groups and the charge characteristics of PDOPA are responsible for the adsorption ability^[32]. In this work, alginate and poly(acrylamide) (PAAm) were employed as the first and the second networks in the DN hydrogels, respectively, which was a classical representative DN hydrogel reported by Suo *et al.*^[33]. PDOPA nanoaggregates were introduced into the DN to improve the adsorption capacity to dyes. In order to facilitate adsorption performance and the recovery ability of the adsorbents after adsorption saturation, here we developed a DN hydrogel preparation method by designing global hydrogel beads with millimeter-scale diameters. The objective of this work is to develop a novel tough hydrogel adsorbent with easy recovery used for high capacity adsorption of dyes from wastewater.

EXPERIMENTAL

Materials and Chemicals

Sodium alginate (SA, viscosity > 0.02 Pa·s, with concentration of 1.0% at 20.0 °C), acrylamide (AAm), methylene-bis-acrylamide (MBAA), ammonium persulphate (APS), CaCl₂, HCl (37%), NaOH, and ethanol (EtOH) were chemical pure and purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). L-3,4-dihydroxyphenylalanine (L-DOPA) was obtained from Sigma Aldrich. Methylene blue (> 90%), methylene orange (> 85%), Azure I and crystal violet (> 90%) were purchased from Aladdin Co. Tris(hydroxymethyl)-aminomethane (Tris, ≥ 99.5%) was obtained from Acros Co. Water with a resistivity of 18 MΩ·cm⁻¹ was prepared using a Millipore Milli-Q system and was used in all experiments.

Preparation of PDOPA Aggregates and DN Hydrogels Beads

L-DOPA was dissolved in tris-buffer solution (50 mmol·L⁻¹, pH = 8.5) with concentration of 0.01 mol·L⁻¹ agitating for more than 24 h at ambient temperature. The solution was rotary-evaporated to be concentrated and then dialyzed to

remove unreacted molecules in ultrapure water. The resulting PDOPA aggregates were obtained by freeze-drying.

Alginate/PAAm DN hydrogel beads were prepared by the following procedure. Firstly, SA and AAm grain (the mass ratio of SA to AAm was 1:6) were dissolved in deionized water, in which the combined amounts of SA and AAm were 14 wt%. The crosslinking agent MBAA, radical initiator APS and accelerator TEMED were added with the molar ratios 0.03 mol%, 0.03 mol% and 0.15 mol% relative to AAm, respectively. After stirring in the ice bath for 3 h, the mixture became a homogeneous and transparent solution. The precursor solution was centrifugated to remove air bubbles. The solution was added dropwise to liquid nitrogen by using a pipet for quickly freezing to hydrogel beads. After the shape and size of the beads were fixed, the beads were quickly mixed with CaSO₄ powder to maintain the shape. Then the as-prepared beads were put in an oven at 60 °C for 3 h, which produced SA/PAAm hydrogels. Secondly, the SA/PAAm hydrogel with CaSO₄·2H₂O powder was soaked in a 0.3 mol·L⁻¹ aqueous solution of CaCl₂ at room temperature for 3 h to obtain alginate/PAAm DN hydrogel beads. Finally, the alginate/PAAm hydrogel beads were separated from suspension and re-dispersed in fresh water to remove residual CaSO₄ and CaCl₂ left in solution.

Similar to alginate/PAAm DN hydrogel beads, PDOPA/alginate/PAAm DN hydrogel beads were prepared as followed. The initial concentration of SA, AAm, MBAA, APS and TEMED was the same as it was used in alginate/PAAm DN hydrogel and that of the PDOPA was varied from 0.2 g·L⁻¹ to 0.5, 1, 2 and 4 g·L⁻¹. The corresponding DN hydrogels are designated as DN-*x*, where *x* represents the concentration of added PDOPA. Because of the radical-scavenging activity of PDOPA in solution, additional APS and TEMED with the molar ratio of 1:1 relatively to PDOPA were used (The composition of each reagents is shown in Table S1, in electronic supplementary information, ESI). The polymerization and crosslinking steps were the same as mentioned before.

Characterizations

Transmission electron microscopy (TEM) imaging was performed on a FEI CM100 at an acceleration voltage of 100 kV. Dynamic light scattering (DLS, Brookhaver, USA) was used to measure the apparent hydrodynamic radius of colloidal aggregates in suspension and zeta potential at different pH values. The operation temperature was 25 °C. The chemical composition of the L-DOPA and PDOPA was analyzed by Fourier transform infrared spectroscopy (FTIR, Vector 22, Germany). Field-emission scanning electron microscopy (FE-SEM) (Hitachi, S-4800) was used to investigate the surface morphologies of DN hydrogel beads. The concentrations of organic dyes in water were determined by UV-Vis absorption spectroscopy, which was carried out on a UV-Vis spectrophotometer (UV5500-PC, Shanghai Jingke Instrument, China). Mechanical tensile tests were carried out by using a tensile machine with a 100 N load cell. The hydrogel was cut into dumbbell shape, with 35 mm length, 2 mm width and gauge length 12 mm and the thickness was measured by a thickness gauge. The clamp

was pulled at a constant velocity of $100 \text{ mm} \cdot \text{min}^{-1}$ at room temperature, where the stress-strain curve was recorded. For the compression tests, the hydrogel was cut into cylindrical shapes with 1 mm diameter and 20 mm height. The compressive stress-strain profile was recorded with $10 \text{ mm} \cdot \text{min}^{-1}$ crosshead speed and the compressive strain was set up to 90%.

Dye Adsorption Experiment

The DN hydrogel beads were lyophilized to dried samples and immersed in 100 mL of distilled water at room temperature until equilibrium was reached. Then the hydrogel beads were filtered by 100-mesh nylon bag and drained to remove excess water. Afterward, the samples were weighed and W_{eq} parameter was calculated from the equation:

$$W_{\text{eq}} = \frac{W_s - W_d}{W_d} \quad (1)$$

where W_s is the swollen sample weight (g) and W_d is the dry sample weight (g).

A series of adsorption experiments were carried out in a thermostatic shaker (TS-2000A, China) at 298 K and $200 \text{ r} \cdot \text{min}^{-1}$ for a given time. The weight of the equilibrium swollen hydrogel beads was fixed at 0.1 g. The hydrogel beads were incubated in 40 mL of aqueous solutions containing methylene blue (MB) as pollutants at concentration of $500 \text{ mg} \cdot \text{L}^{-1}$. The pH of the aqueous solutions was adjusted to 6.0. The concentration of MB solution was analyzed by a UV-Vis spectrophotometer *via* measuring the absorbance changes at a wavelength of 668 nm. At desired time intervals, the temporal adsorption uptake (q_t , $\text{mg} \cdot \text{g}^{-1}$) of dye can be correlated with adsorption time (t , min) as below equation:

$$q_t = \frac{(c_0 - c_t)V}{W} \quad (2)$$

where c_0 ($\text{mg} \cdot \text{L}^{-1}$) is the initial concentration of the dye in water, c_t ($\text{mg} \cdot \text{L}^{-1}$) is the dye concentration in water at a given time (t , min), V (L) is the volume of the aqueous solution of the pollutant, and W (g) is the mass of the dried hydrogel beads.

The equilibrium adsorption uptake (q_e , $\text{mg} \cdot \text{g}^{-1}$) of the hydrogel beads can be calculated from the following equation:

$$q_e = \frac{(c_0 - c_e)V}{W} \quad (3)$$

where c_e ($\text{mg} \cdot \text{L}^{-1}$) is the MB concentration at equilibrium.

In order to study the adsorption isotherm, batch adsorption experiments were conducted with the initial MB concentration of $250\text{--}1000 \text{ mg} \cdot \text{L}^{-1}$ at the temperature of 298 K.

After the equilibrium adsorption was reached, the hydrogel beads were separated from the pollutants solution and washed in pure water to remove excess dyes. Then the beads were incubated in the mixture of ethanol (1 mL) and pH 3 acidic aqueous solutions (20 mL). The concentrations (c_d^t , $\text{mg} \cdot \text{L}^{-1}$) of the dye released into water/ethanol mixtures at different desorption time (t_d , min) were determined by

UV-Vis spectroscopy. The desorption efficiency (E_d^t) of the hydrogel beads after a certain time t_d can be calculated as below

$$E_d^t = \frac{c_d^t V_d}{q_e W} \quad (4)$$

where V_d is the solution volume used for desorption, W is the weight of dried DN hydrogel beads.

RESULTS AND DISCUSSION

Synthesis and Characterization of PDOPA Aggregates

In a weak alkaline condition, L-DOPA was found to undergo self-oxidization and self-assembly process in aqueous solutions and form aggregates (Fig. 1a). With the addition of L-DOPA into tris-buffer, the color of the solution turned to little pink and became completely black after stirring at ambient temperature for 24 h. DLS experiment was conducted to measure the size and surface zeta potential of PDOPA aggregates. The result shows that the size profile of samples consists of two major peaks with the value of 18 and 930 nm (seen in Fig. S1A, in ESI). As revealed by TEM images of PDOPA (seen in Fig. 1b), the morphology of the resulting PDOPA aggregates is complex with various size aggregates, which is coincident with DLS result. Though there are aggregates with size more than $1 \mu\text{m}$ from the view of TEM images, it is found that no precipitates are observed after centrifugation of the resulting PDOPA solution. In addition, there is no retention left after filtrating PDOPA solution through a $0.22 \mu\text{m}$ filter, suggesting that well-dispersed PDOPA products were obtained after reaction. It can be explained that the carboxyl group in L-DOPA enhance the solubility of PDOPA aggregates through ionic interaction in aqueous solutions. The surface zeta potential result shown in Fig. 1(b) indicates that PDOPA aggregates were negatively charged. Fig. 1(c) shows the FTIR spectra of L-DOPA and PDOPA. There is a remarkable change in L-DOPA in the FTIR spectra after self-oxidation and self-assembly into PDOPA. The absorption peaks of PDOPA broaden and become not separable from each other, which is similar to the spectra of polydopamine (PDA). The peaks at 1620 and 1510 cm^{-1} of PDOPA are attributed to the overlap of C=C resonance vibrations in the aromatic ring, C=O resonance vibrations in the $-\text{COO}^-$ group, and the N-H bending vibrations, which proves the fabrication of PDOPA from self-oxidation and self-assembly of L-DOPA. When introducing PDOPA into DN hydrogel, an additional peak appears at 1650 cm^{-1} in ATR-FTIR spectrum, which is derived from PDOPA (details seen in Fig. S1B, in ESI). Furthermore, L-DOPA and PDOPA powders were characterized by XPS analysis. The high-resolution spectrum of N element in Fig. 1(d) shows that N element at 401.9 eV in L-DOPA is mainly assigned for the $-\text{NH}_3^+$ species, indicating that primary amine is protonated before oxidation. After oxidation and self-polymerization, new peaks are clearly observed and the N 1s signal is divided into two major peaks at 401.9 and 400.1 eV , which could be attributed to $-\text{NH}_3^+$ and $-\text{NH}^-$ species, respectively. The molar ratio of the $-\text{NH}_3^+$ to $-\text{NH}^-$ species is calculated to be 1.4:1,

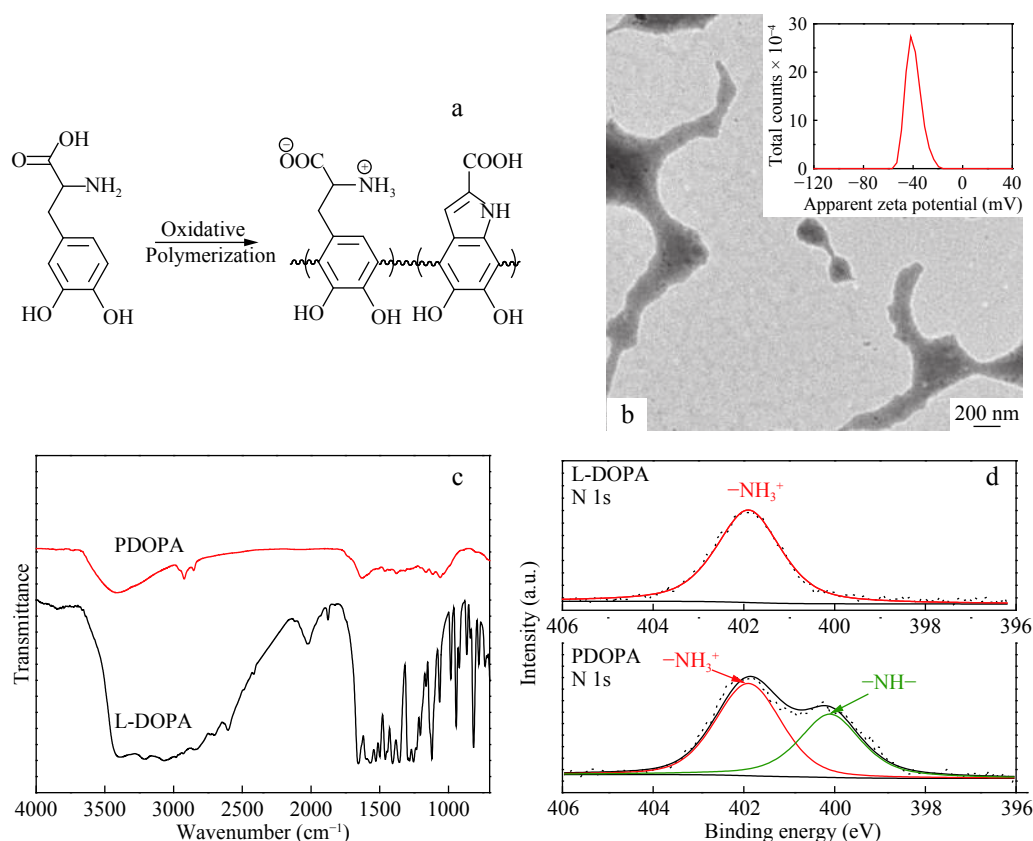


Fig. 1 (a) Schematic illustration of the self-polymerization of L-DOPA into PDOPA; (b) TEM image of PDOPA in solution. Scale bar is 200 nm; The inset is the zeta potential result of PDOPA; (c) FTIR result of nascent L-DOPA and PDOPA; (d) High-resolution XPS spectra of the N 1s peaks of L-DOPA (upper panel) and PDOPA (lower panel)

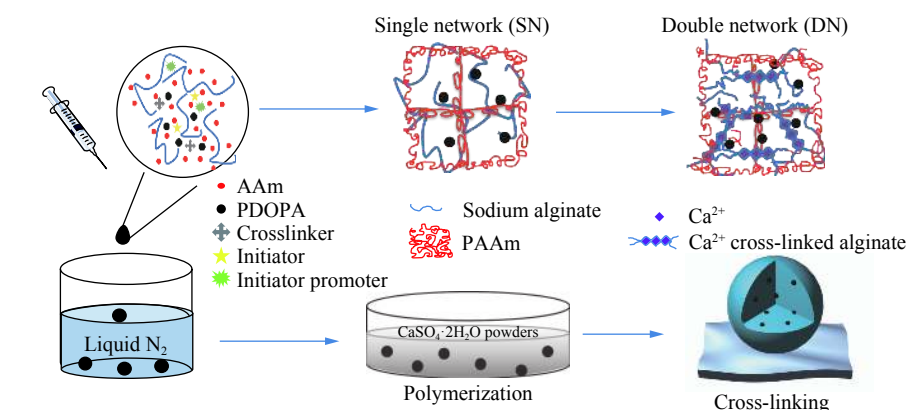
indicating that 41.6% of the original primary amine groups were reacted to form indole-like structures through Michael-addition cyclization. High resolution spectra of C element were also fitted using three components with binding energies of 284.6, 286.0, and 288.4 eV, corresponding to C=C/C-C, C-N/C-O, and C=O/O-C=O, respectively (Fig. S2B, in ESI). The calculated molar ratios of the C=C/C-C, C-N/C-O, and C=O/O-C=O were 5:3.2:1 and 4.5:4.9:1 for L-DOPA and PDOPA, respectively. The increase of the molar percentage of C-N/C-O peak also indicates the intramolecular cyclization of amino group in PDOPA.

Fabrication of Alginate/PAAm DN Hydrogel Beads and PDOPA/Alginate/PAAm DN Hydrogel Beads

Hydrogels are a network of polymer chains, which contain much water. Compared with some adsorbents like active carbon, graphene, and zeolite *etc.*, it is beneficial to use hydrogels as adsorbents or adsorbent carriers for the easy separation and reuse after water decontamination. Nevertheless, the mechanical toughness of hydrogels is always drastically weakened after saturation adsorption, which may cause the crush of hydrogels and the release of adsorbents into water. Herein, alginate/PAAm DN hydrogel beads and PDOPA/alginate/PAAm DN hydrogel beads were prepared (shown in the inset of Figs. 2a and 2b). The precursor solution, consisting of PDOPA, SA and AAm, was

stable after mixing and dissolving all the components. There was no sedimentation or aggregation after centrifugation or long time standing, which is important for subsequent polymerization and crosslinking reaction. Interactions, like ionic coordination or hydrogen bonding, between PDOPA and polymer network made sure the good compatibility between each component. It is well known that DN hydrogels show better mechanical performance after swelling than common hydrogels do, which ensures the durability of the adsorbents during adsorption and desorption process. The key procedure for preparation of DN hydrogel beads was using CaSO₄ grains to hold the shape of beads before polymerizing the AAm monomer by heating. CaSO₄ here acted as a mild cross-linker to encapsulate the hydrogel beads so that the beads were still spherical in shape at high temperature. Other powders like CaCl₂ grains were not selected because the second network monomer together with water would be separated from the alginate network. It can be explained that CaCl₂ has a good solubility in water, and the frozen beads would lose its water and dissolved monomer to the surrounding CaCl₂ during heating process. The final alginate/PAAm DN hydrogel beads were fabricated by Ca²⁺ ion cross-linking of the guluronic acid (G unit) blocks in alginate (Scheme 1)^[33].

As prepared hydrogel beads were 2–3 mm large in size, as shown in inset pictures in Fig. 2. The color of



Scheme 1 Schematic illustration for preparation of PDOPA-containing DN hydrogel beads

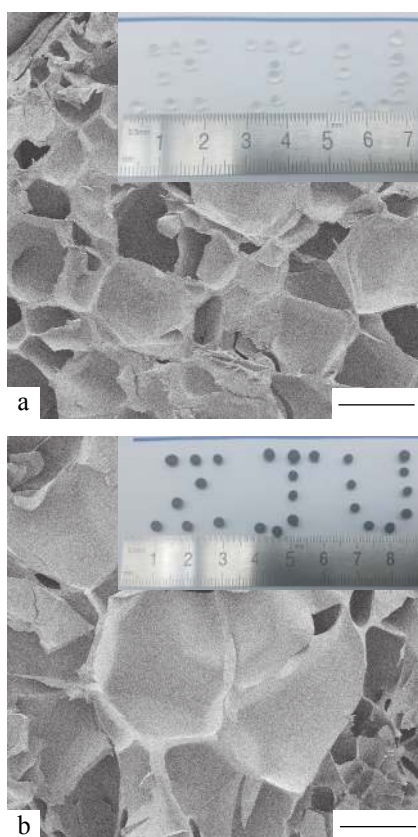


Fig. 2 SEM images of the cross section of the DN hydrogel beads loaded (a) without and (b) with PDOPA, respectively. The insets in (a) and (b) show the photographs of the corresponding hydrogel beads. Scale bar is 200 μm .

PDOPA/alginate/PAAm DN hydrogel beads turned to black with similar size of DN hydrogel beads. The insight morphology of lyophilized hydrogel beads was observed by SEM (Fig. 2). Micro-pores in hydrogels formed here were mainly caused by the sublimation of ice crystal during freeze-drying step^[34]. No obvious large aggregates were observed in SEM images, indicating a relatively uniform dispersion of PDOPA in hydrogel network. It is reported that mussel-inspired surface modification method could improve the interfacial compatibility when blending polymer matrix and additives, where most modified nanomaterials avoid

aggregation^[35, 36]. PDOPA, a representative of catechol-based modification products, exhibits good compatibility with DN matrix based on strong affinity of catechol group in PDOPA^[37–39]. It is shown in Fig. S3 (in ESI) that DN hydrogel beads were tough enough to recover to its original shape. Alginate single network (SN) hydrogel beads were squashed when using tweezers to grasp the beads and could not recover to its former state, indicating the DN hydrogel beads had better mechanical properties than the SN hydrogels.

Since PDOPA-based materials have the radical scavenging activities^[19, 40], it is necessary to handle the issue that radical initiator would be insufficient to initiate the polymerization of AAm when introducing PDOPA. Herein, additional initiator and initiator accelerator with a certain ratio to PDOPA were added to counteract this effect^[41]. However, higher initiator concentration would cause a low molecular weight of PAAm, which eventually limited the mechanical strength of prepared DN hydrogels. The amounts of the PDOPA up to 4 g·L⁻¹ were restricted in this work to obtain relatively tough hydrogel beads.

To test the stability of DN hydrogel beads, they were incubated in water and stirred at 600 r·min⁻¹ for 7 days. Both alginate/PAAm and PDOPA/alginate/PAAm DN hydrogel beads remained intact and the solution remained clear and transparent. The incubation solution was then analyzed by UV spectroscopy after the removal of DN hydrogel beads. The absorption peak at 280 nm, attributed to PDOPA, was negligible in the resulting aqueous solutions, which indicated that PDOPA was firmly incubated in the hydrogel beads. It is suggested that the physical embedment of PDOPA into hydrogel and chemical affinity between PDOPA and PAAm or alginate chain contributed to such good stability^[42, 43]. It is reported that the swelling ratio of hydrogels significantly affects the mechanical properties of hydrogels^[44]. As shown in Fig. 3(a), the DN hydrogel beads had a lower swelling ratio than the SN hydrogel beads. Lower swelling ratio reveals that the swelling behavior is suppressed and it is helpful to maintain both shape and mechanical strength. The addition of PDOPA suppressed the swelling ratio little, mainly because (1) possible ionic bonding between PDOPA and Ca²⁺, and (2) hydrogen bonding between PDOPA and DN hydrogel could provide

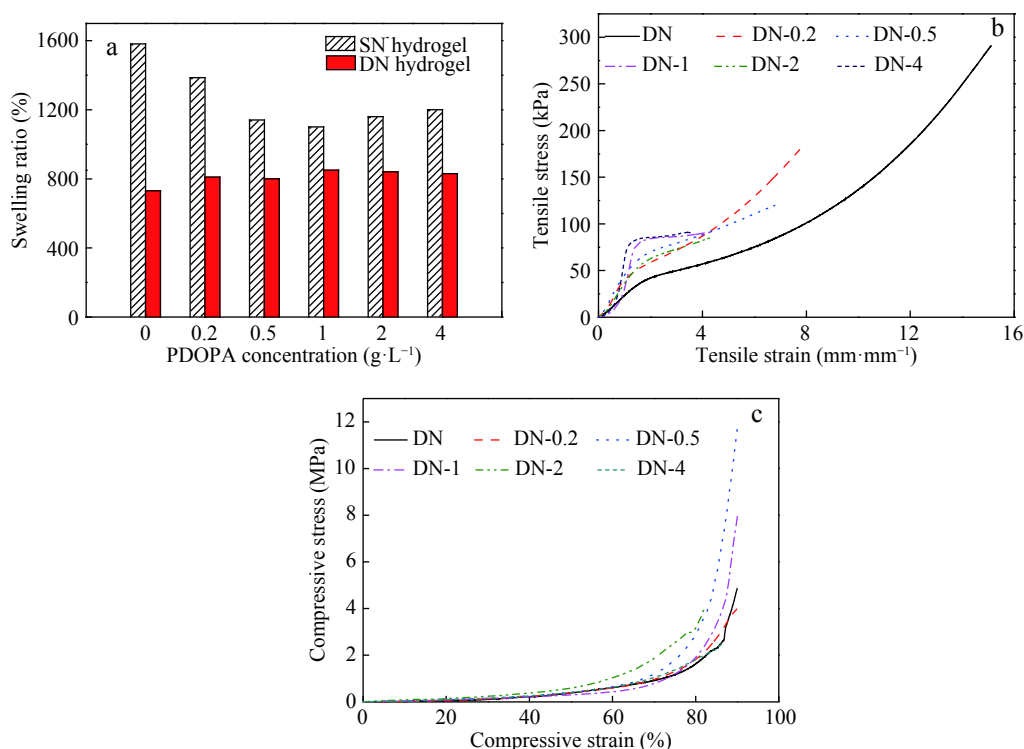


Fig. 3 (a) Swelling ratios of the SN and DN hydrogel with different PDOPA contents; (b) Tensile and (c) compressive stress-strain profiles of the DN hydrogels

additional interactions compared with neat DN hydrogel, thus decreasing the swelling ratio.

Mechanical tests were conducted to evaluate the toughness of the prepared hydrogels. The inevitable shrinkage of alginate SN hydrogel cross-linked by Ca²⁺ made the hydrogel lose its regular shape. As expected, alginate/PAAm DN hydrogel and PDOPA-containing DN hydrogel exhibited great enhancement of tensile strength compared to each SN hydrogel (seen in Fig. S4, in ESI). The alginate/PAAm hydrogel exhibited a strength of 296.6 kPa and its stretch reached 15.1, which is similar to that of reported DN hydrogel (Fig. 3b)^[45]. The strength of SN alginate hydrogel and PAAm hydrogel was 2.6 and 11.9 kPa, respectively, and stretch reached 1.5 and 7.0, respectively (Fig. S4, in ESI). Upon the introduction of PDOPA into the DN hydrogel, the mechanical strength decreased as the PDOPA concentration increased. It can be explained that the additional amount of initiator and PDOPA slightly inhibited the polymerization of AAm to a high molecular weight, which in turn decreased the strength. However, the mechanical performance of the DN hydrogel with PDOPA was much more superior than that of SN hydrogel. In addition, both curves exhibited yielding-like behavior, which indicated the damage of the first network during stretching process^[46]. Moreover, compressive test shown in Fig. 3(c) also indicated that the DN hydrogels had splendid resiliency and elasticity. Both DN hydrogel in cylinder or bead forms possessed the ability to rapidly recover to their former shape upon removal of the external force (Fig. S5, in ESI).

Dye Adsorption Characteristics

To investigate the adsorption properties of the

PDOPA/alginate/PAAm DN hydrogel beads, cationic dye like methylene blue (MB), Azure I, and crystal violet (CV) were used, where MB was selected as a target pollutant. Other organic molecules, like anionic dye methyl orange (MO) and neutral molecule Vitamin B12 (VB12) (both organic molecular structures can be seen in Fig. S6, in ESI) were also used to conduct adsorption experiment. All the adsorption experiments were carried out at pH 6. In comparison, alginate SN hydrogel bead and PDOPA/alginate SN hydrogel beads were used to adsorb the MB at the concentration of 500 ppm. As shown by Fig. 4(a), after equilibrium adsorption, the MB adsorption uptake from pristine alginate SN bead reached 814 mg·g⁻¹, which indicated that the alginate network made contributions to cationic dye adsorption process. The introduction of PDOPA would enhance the equilibrium adsorption uptakes of the hydrogel beads toward MB. With the increasing amount of PDOPA, the adsorption uptakes increased as well. However, as we mentioned before, the mechanical strength of the SN hydrogel beads should be taken into consideration as the beads are fragile after equilibrium adsorption. For DN hydrogel, the equilibrium adsorption uptake reached 1064 mg·g⁻¹, which is slightly higher than that of SN hydrogel. Similarly, introduction of PDOPA increased the adsorption uptake. The pseudo-first-order (seen in Figs. 4a and 4c) and pseudo-second-order kinetic models (seen in Figs. 4b and 4d) were used to analyze the experimental data and the calculated q_t values were plotted as a function of t to determine the adsorption kinetics model. The correlation coefficient (R^2) was considered to evaluate the agreement between the experimental results and the two proposed

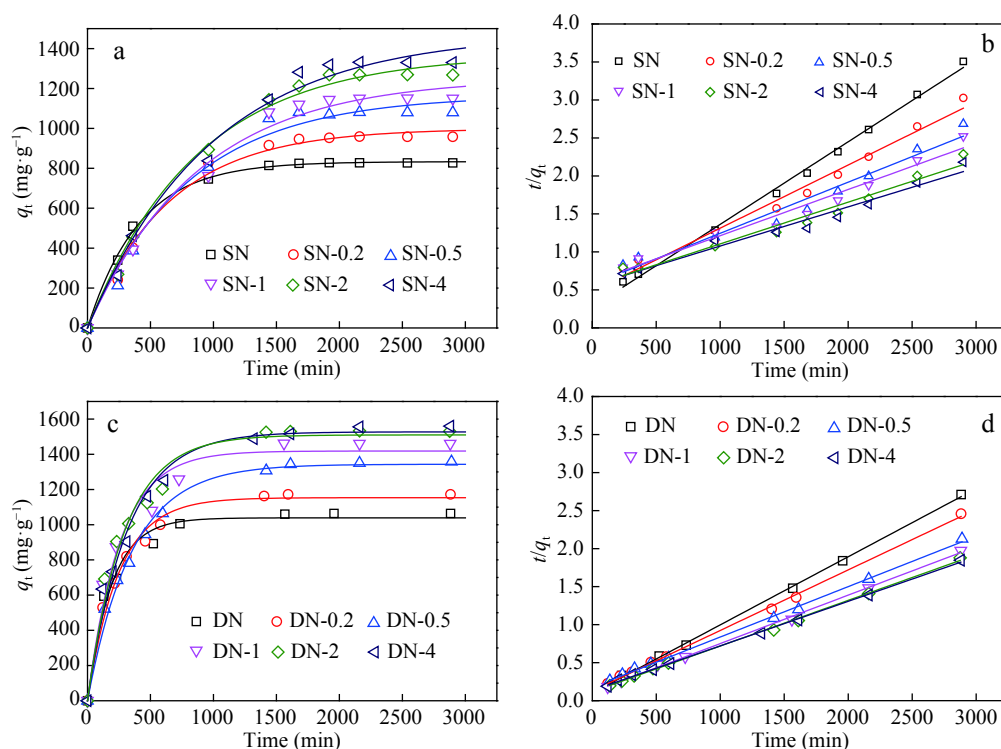


Fig. 4 Kinetics profile of the adsorption of MB (open symbols) by SN hydrogel beads fitted by the (a) pseudo-first-order (solid curves) and (b) the pseudo-second-order (solid curves); Kinetics profile of the adsorption of MB (open symbols) by DN hydrogel beads fitted by the (c) pseudo-first-order (solid curves) and (d) fitted by the pseudo-second-order (solid curves), respectively

models (Eqs. 5 and 6).

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (5)$$

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (6)$$

where q_e and q_t represent the adsorption capacity of dye at equilibrium and any time t , respectively. The parameters k_1 and k_2 are the rate constants of the pseudo-first-order and pseudo-second-order models, respectively.

The calculated kinetic parameters (k_1 , k_2 , $q_{e,cal}$) and correlation coefficient R^2 are shown in Table 1. It can be concluded that the pseudo-second-order kinetics model fits the experimental data better with higher coefficient of determination (R^2) than pseudo-first-order kinetics model does, suggesting that chemisorption is the rate-determining step for the adsorption of MB by the hydrogel beads^[47].

Langmuir isotherm and Freundlich isotherm were used to evaluate the adsorption equilibrium as in Eqs. (7) and (8), respectively.

$$\frac{c_e}{q_e} = \frac{c_e}{q_m} + \frac{1}{K_L q_m} \quad (7)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln c_e \quad (8)$$

where K_L ($L \cdot g^{-1}$) is the Langmuir constant of adsorption, and q_m is the maximum adsorption capacity based on the Langmuir model; K_F is the Freundlich constants of adsorption and n is heterogeneity factor. The fitting results are listed in Table 2. The values of R^2 suggest that the fitness of Langmuir model to the experimental data was better than that of Freundlich model (seen in Figs. 5a and 5b). According to the Langmuir isotherm model, adsorption occurs as homogeneous monolayer coverage on surface of the adsorbents^[48]. Moreover, the maximum adsorption capacity could be estimated by this model, and DN hydrogel exhibited $1124 \text{ mg} \cdot \text{g}^{-1}$ for the maximum adsorption uptake. This value increased with increasing PDOPA content, and reached $1820 \text{ mg} \cdot \text{g}^{-1}$ for DN-4 hydrogel bead. The

Table 1 The experimental results for the adsorption of MB by DN and PDOPA-containing DN hydrogel beads and calculated $q_{e,cal}$ based on fitting the adsorption kinetics with pseudo-first-order and pseudo-second-order models

MB	$q_{e,exp} \text{ (mg} \cdot \text{g}^{-1}\text{)}$	Pseudo-first-order			Pseudo-second order		
		$q_{e,cal} \text{ (mg} \cdot \text{g}^{-1}\text{)}$	$k_1 \text{ (min}^{-1}\text{)}$	R^2	$q_{e,cal} \text{ (mg} \cdot \text{g}^{-1}\text{)}$	$k_2 \times 10^6 \text{ (g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}\text{)}$	R^2
DN	1064.1	1039.0	0.0053	0.981	1116.2	7.96	0.999
DN-0.2	1172.6	1153.5	0.0040	0.985	1255.5	5.01	0.998
DN-0.5	1357.8	1343.4	0.0028	0.992	1508.8	2.52	0.998
DN-1	1460.4	1418.6	0.0039	0.967	1570.0	3.56	0.998
DN-2	1530.3	1510.0	0.0035	0.977	1665.6	3.05	0.998
DN-4	1559.8	1527.2	0.0032	0.985	1707.4	2.55	0.999

Table 2 The summary of parameters derived from the Langmuir and Freundlich isotherms for MB adsorption by hydrogel beads

	Langmuir model			Freundlich model		
	q_m (mg·g ⁻¹)	K_L (L·mmol ⁻¹)	R^2	K_F (mg·g ⁻¹ ·L ^{1/n} ·mmol ^{1/n})	n (g·L ⁻¹)	R^2
DN	1123.8	0.082	0.998	395.4	5.96	0.829
DN-0.2	1289.7	0.062	0.994	584.1	7.97	0.733
DN-0.5	1524.9	0.051	0.999	603.2	6.76	0.912
DN-1	1717.8	0.053	0.996	603.2	5.89	0.892
DN-2	1802.6	0.068	0.999	745.8	6.85	0.698
DN-4	1819.5	0.070	0.999	468.8	4.18	0.736

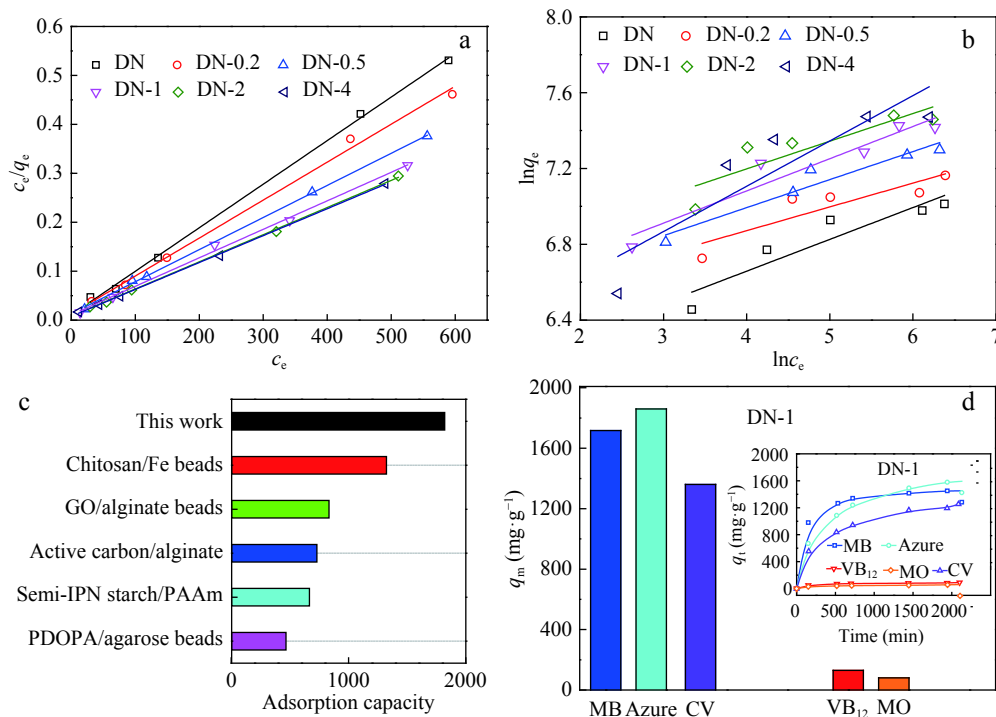


Fig. 5 (a) Langmuir and (b) Freundlich isotherms fitting for varied concentration of MB adsorption on hydrogel beads (Plot: experimental results. Line: fitting curves); (c) Comparison of the q_m values fitted with Langmuir model for the adsorption of MB by the adsorbents reported in literatures^[32, 49–52]; (d) The q_m values for the adsorption of different kinds of dyes by DN-1 adsorbent and the insight in (d) is adsorption kinetic for these dyes (each dye concentration: 500 ppm)

maximum adsorption q_m value of the MB on the DN hydrogel beads was higher than that of the SN hydrogel beads (shown in Table 2 and Table S2, in ESI), indicating that DN system had not only improved mechanical strength, but also the higher adsorption capacity. The adsorption value of MB is higher than that of the other adsorbents with similar functional groups reported in the literatures *e.g.*, PDOPA/agarose beads^[32], active carbon/alginate^[49], GO/alginate SN hydrogel beads^[50], semi-IPN starch/PAAm hydrogel^[51] and chitosan/Fe-hydroxyapatite beads^[52] (Fig. 5c). In addition, the PDOPA-containing DN hydrogel beads also exhibited adsorption of other positively charged dyes like crystal violet (CV) and Azure I with similar adsorption performance (Fig. 5d), which indicates that the hydrogel beads can be used in cationic dyes adsorption process.

In order to investigate the adsorption mechanism, zeta potential test was conducted to measure the surface charge of the alginate SN hydrogel, PDOPA aggregates, alginate/PAAm DN hydrogel and PDOPA/alginate/PAAm DN hydrogel. As shown in Fig. 6(a), the zeta potentials of the

alginate SN and the alginate/PAAm DN hydrogel were -11.2 and -13.6 mV, respectively, showing weakly negative surface charge of SN and DN hydrogel in ambient condition. This value for PDOPA was -37.3 mV, exhibiting more charges than that of SN or DN system. Potential for PDOPA/alginate/PAAm hydrogel was about -21.8 mV, meaning not all the PDOPA was motivated to the surface of the hydrogel. We also investigated the influence of various concentrations of NaCl on adsorption performance. As shown in Fig. 6(b), lower concentration of NaCl had little effects on the adsorption performance, which resulted from a balance between rising active sites derived from ion exchanging and electrostatic screening effects. With higher concentration of NaCl, the adsorption of MB dramatically decreased, which indicates that the electrical interaction between dyes and hydrogel beads is the main adsorption driving force. In addition, ATR-FTIR spectra of DN-1 film and MB loaded DN-1 film were investigated, respectively. After adsorption of MB onto the hydrogel, the appearance of the new band at 880 cm^{-1} is attributed to the adsorbed MB

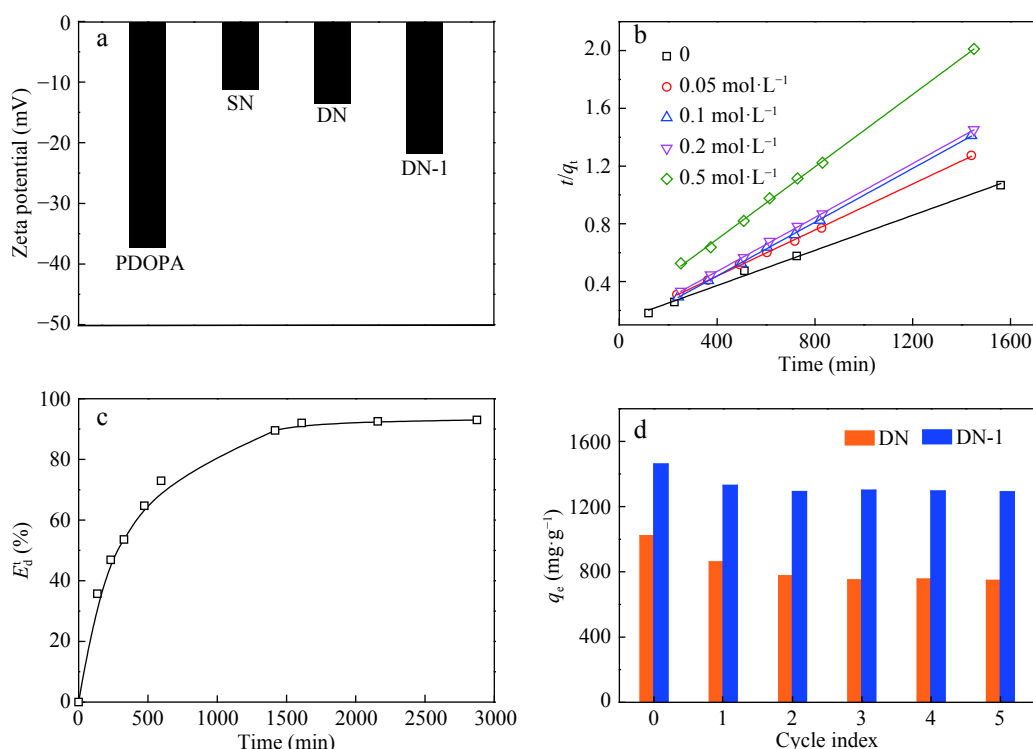


Fig. 6 (a) Surface zeta potential of PDOPA, SN, DN and DN-1 hydrogel at pH 6; (b) The effect of additional salt on the kinetic profile of the MB adsorption by DN-1 hydrogel; (c) Kinetic profile of the desorption efficiency (E_d) of MB by DN-1 hydrogel with various desorption time. The incubation solution consisted of 20 mL ethanol and 20 mL pH 3 acidic aqueous solutions; (d) Regeneration of the DN-1 hydrogel and its adsorption performance on different reuse cycles. For each adsorption test, the initial concentration of the organic dye was 500 mg·L⁻¹.

molecules (seen in Fig. S7, in ESI). Compared to original DN-1 hydrogel, absorption bands of DN-1 at 1670 and 1725 cm⁻¹ shifted to 1700 cm⁻¹, indicating the C=O and —COO⁻ stretching vibration changed due to the ionization of carboxyl group in hydrogel. These results further confirm that the electrostatic attraction is the main adsorption mechanism of MB onto the adsorbent.

The reusing and recycling of an adsorbent is an important feature that should be taken into consideration for practical application. After adsorption of the MB, the hydrogel beads were incubated with alcohol and acidic aqueous solutions to remove the adsorbed dyes, as shown in Fig. 6(c). The desorption efficiencies of varied PDOPA concentration for MB were averaged to be about 90% after 12 h incubation. In the next run, the adsorption uptake changed slightly compared to that of the initial hydrogel beads, which may be possibly due to the arising active site during desorption process. However, the stress-stretch curve and hysteresis curves of DN-1 hydrogel after desorption process shown in Fig. S8 (in ESI) indicated that the hydrogel beads still exhibited tough mechanical strength. The hysteresis in DN hydrogel suggested that the divalent ionic cross-links still existed and ensured strength, while Na-alginate/PAAm hydrogel always shows negligible hysteresis^[45]. Compared with freshly prepared ones, the regenerated hydrogel beads exhibited slight adsorption uptake decrease at least for five times adsorption/desorption cycles (Fig. 6d), thus guaranteeing the excellent reusability.

CONCLUSIONS

A kind of tough PDOPA-containing DN hydrogel beads with quite high capacity of dye adsorption was demonstrated. The DN architecture brought not only high mechanical strength, but also better adsorption ability to the hydrogel beads. The incorporation of PDOPA with an appropriate amount into the hydrogels showed advantageous to the promotion of the adsorption ability. The global shape with millimeter-scale diameter for the hydrogel adsorbents facilitated the recovery and regeneration after adsorption saturation. The synergistic effects between PDOPA and DN architecture were responsible for the quite high capacity of dye adsorption. The mechanism of dye adsorption for the hydrogel beads was attributed to the electrical interaction between dyes and hydrogels. The saturated hydrogel beads could be regenerated by simple rinsing in acidic water and the adsorption capacity was maintained after several times of adsorption and desorption cycles. Here the reported fabrication technique of the PDOPA-containing DN hydrogel beads is easily scaled up for practical applications. This work develops a novel and high-performance adsorbent used for the treatment of textile dyeing wastewater.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-018-2163-2>.

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