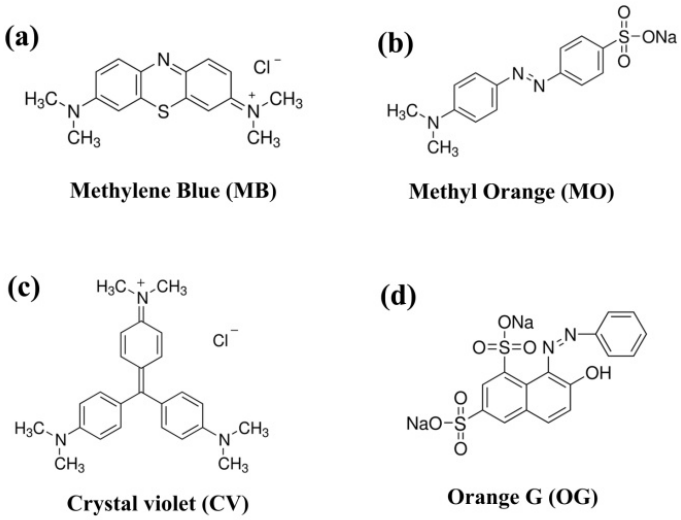
Confined Flocculation of Ionic Pollutants by Poly(L-Dopa)-based Polyelectrolyte Complexes in Hydrogel Beads for Three-Dimensional, Quantitative, Efficient Water Decontamination

Li Yu, Xiaokong Liu,* Weichang Yuan, Lauren Joan Brown, and Dayang Wang*
Ian Wark Research Institute, University of South Australia, Mawson Lakes, SA 5095, Australia
E-mail: xiaokong.liu@unisa.edu.au; dayang.wang@unisa.edu.au

Supporting Information



Scheme S1. Schematic sketch of the molecular structures of MB, MO, CV and OG.

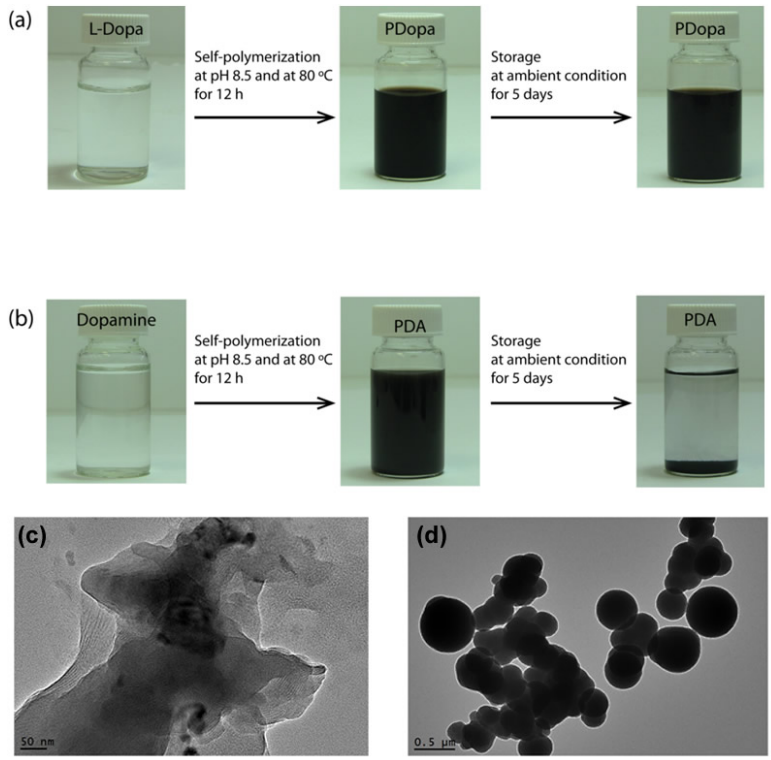
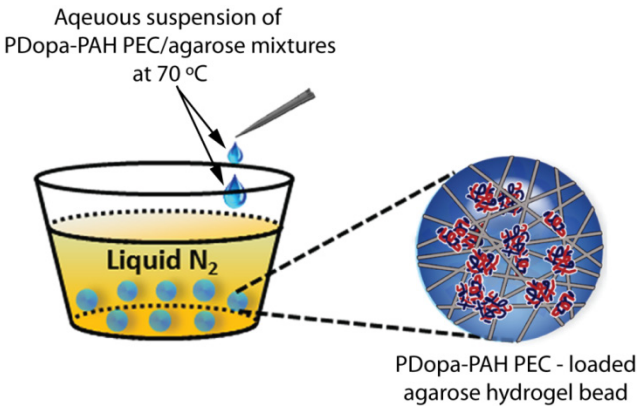


Figure S1. (a,b) Photographs of the glass vials of the aqueous solutions of L-Dopa (a) and dopamine (b) over the course of self-polymerization. The aqueous solutions of the monomers are initially prepared at ambient temperature and at pH 2 (left panels). After the pH is adjusted to 8.5, the solutions are heated at 80°C for 12 h to implement self-polymerization (middle panels). Afterwards, the resulting black solutions are cooled down to ambient temperature and stored for 5 days (right panels). (c,d) TEM images of the resulting PDopa (c) and PDA (d).



Scheme S2. Schematic illustration of preparation of PDopa-PAH PEC–loaded agarose hydrogel beads by dropwise adding the hot (70 °C) aqueous suspensions of the mixture of PDopa-PAH PECs and agarose into liquid nitrogen.

Table S1. Summary of the compositions of $PDopa_{3.5}$-PAH_1 PEC-loaded agarose hydrogel beads prepared from the aqueous suspensions of PEC/agarose mixtures. The suspension volume is 1L.

Agarose		$PDopa_{3.5}$-PAH_1 PECs		Total solid content (wt%)
Concentration (wt%)	Amount (g)	Concentration (mM)	Amount (g)	
1.5	15	1	0.17	1.49
1.5	15	2	0.35	1.51
1.5	15	5	0.87	1.56
1.5	15	10	1.74	1.65
1.5	15	50	8.7	2.32
1.5	15	100	17.4	3.14

Table S2. Summary of the compositions of $PDopa_1$-$PAH_{3.5}$ PEC-loaded agarose hydrogel beads prepared from the aqueous suspensions of PEC/agarose mixtures. The suspension volume is 1L.

Agarose		$PDopa_1$-$PAH_{3.5}$ PECs		Total solid content (wt%)
Concentration (wt%)	Amount (g)	Concentration (mM)	Amount (g)	
1.5	15	1	0.12	1.49
1.5	15	2	0.22	1.50
1.5	15	5	0.58	1.53
1.5	15	10	1.17	1.59
1.5	15	50	5.83	2.04
1.5	15	100	11.65	2.60

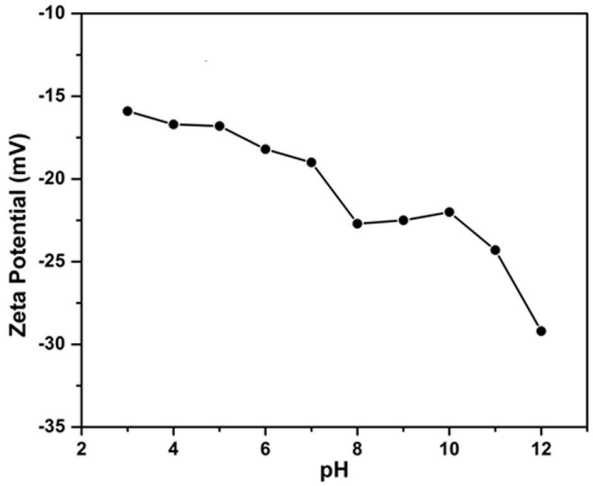


Figure S2. Plot of the Zeta potential value of PDopa versus pH in water.

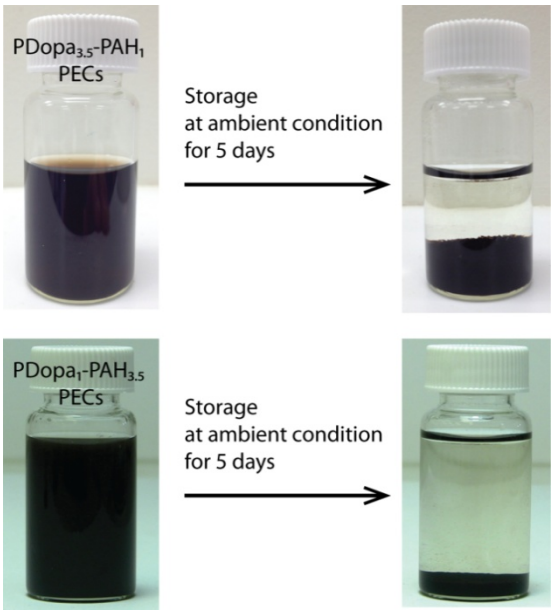


Figure S3. Photographs of the aqueous suspensions of PDopa-PAH PECs shot immediately after the aqueous solutions of the PDopa and PAH are mixed (left panels) and after the resulting PEC suspensions are stored at ambient condition for 5 h (right panels).

Calculation details of the PDopa-to-PAH molar ratio based on the N 1s signals of the XPS spectra of PDopa-PAH PECs.

The N 1s signals in the XPS spectra of both PDopa and PDopa-PAH PECs can be deconvoluted into three peaks at ca. 402 eV, ca. 400 eV, and ca. 399 eV, respectively, arising from $–NH_3^+$, –NH–, and $–NH_2$ species. The area fraction of these three peaks with respect to the whole N 1s signals can be used to estimate the atomic fraction of these three species, which are denoted as A_{PDopa}^{NH3}, A_{PDopa}^{NH}, and A_{PDopa}^{NH2} for PDopa ($A_{PDopa}^{NH3} + A_{PDopa}^{NH} + A_{PDopa}^{NH2} = 1$) and A_{PEC}^{NH3}, A_{PEC}^{NH}, and A_{PEC}^{NH2} for PDopa-PAH PECs ($A_{PEC}^{NH3} + A_{PEC}^{NH} + A_{PEC}^{NH2} = 1$). On the other hand, the N 1s signal in the XPS spectrum of PAH can be deconvoluted only into two peaks centered at ca. 402 eV and ca. 399 eV for $–NH_3^+$ and $–NH_2$ species; their peak area fraction with the whole N 1s signal are denoted as A_{PAH}^{NH3} and A_{PAH}^{NH2} ($A_{PAH}^{NH3} + A_{PAH}^{NH2} = 1$).

Obviously, only the –NH– species of the PDopa components contributes the A_{PEC}^{NH} of the PDopa-PAH PECs, denoted as $A_{PEC}^{NH/PDopa}$, namely, $A_{PEC}^{NH/PDopa} = A_{PEC}^{NH}$. However, the $–NH_3^+$ and $–NH_2$ species of both the PDopa and PAH components contribute the A_{PEC}^{NH3} and A_{PEC}^{NH2} of the PECs, which are denoted as $A_{PEC}^{NH3/PDopa}$ and $A_{PEC}^{NH2/PDopa}$ for the PDopa contribution and as $A_{PEC}^{NH3/PAH}$ and $A_{PEC}^{NH2/PAH}$ for the PAH contribution. For a given $PDopa_x$-PAH_y PEC, thus:

$$x/y = \frac{A_{PEC}^{NH/PDopa} + A_{PEC}^{NH3/PDopa} + A_{PEC}^{NH2/PDopa}}{A_{PEC}^{NH3/PAH} + A_{PEC}^{NH2/PAH}} \quad \text{(s1)}$$

The $PDopa_x$-PAH_y PECs are formed via electrostatic interactions without change in the PDopa molecular structure, so:

$$A_{PEC}^{NH/PDopa} : A_{PEC}^{NH3/PDopa} : A_{PEC}^{NH2/PDopa} = A_{PDopa}^{NH} : A_{PDopa}^{NH3} : A_{PDopa}^{NH2} \quad \text{(s2)}$$

As such, we expect:

$$A_{PEC}^{NH3/PDopa} = A_{PEC}^{NH} \cdot \frac{A_{PDopa}^{NH3}}{A_{PDopa}^{NH}} \quad \text{(s3)}$$

$$A_{PEC}^{NH2/PDopa} = A_{PEC}^{NH} \cdot \frac{A_{PDopa}^{NH2}}{A_{PDopa}^{NH}} \quad \text{(s4)}$$

Also, it is obvious that

$$A_{PEC}^{NH3/PAH} = A_{PEC}^{NH3} - A_{PEC}^{NH3/PDopa} \quad \text{(s5)}$$

$$A_{PEC}^{NH2/PAH} = A_{PEC}^{NH2} - A_{PEC}^{NH2/PDopa} \quad \text{(s6)}$$

By taking Equations (s3-s6) into account, Equation s1 can be written as below:

$$x/y = \frac{A_{PEC}^{NH} + A_{PEC}^{NH} \cdot \frac{A_{PDopa}^{NH3}}{A_{PDopa}^{NH}} + A_{PEC}^{NH} \cdot \frac{A_{PDopa}^{NH2}}{A_{PDopa}^{NH}}}{\left(A_{PEC}^{NH3} - A_{PEC}^{NH} \cdot \frac{A_{PDopa}^{NH3}}{A_{PDopa}^{NH}}\right) + \left(A_{PEC}^{NH2} - A_{PEC}^{NH} \cdot \frac{A_{PDopa}^{NH2}}{A_{PDopa}^{NH}}\right)} \quad \text{(s7)}$$

Equation s7 can be rearranged as below:

$$y/x = (A_{PEC}^{NH3}+A_{PEC}^{NH2}) \cdot A_{PDopa}^{NH}/A_{PEC}^{NH} - (A_{PDopa}^{NH3} + A_{PDopa}^{NH2}) \qquad \text{(s8)}$$

From the N 1s signal of the XPS spectrum of PDopa (Figure 2a), it is obtained that A_{PDopa}^{NH} = 79.32%, A_{PDopa}^{NH3}= 10.51%, and A_{PDopa}^{NH2} = 10.17%. In the case of $PDopa_{3.5}$-PAH_1 PECs, the N 1s signals of their XPS spectra reveals that A_{PEC}^{NH} = 57.73%, A_{PEC}^{NH3} = 27.45%, and A_{PEC}^{NH2} = 14.82%. According to Equation s8 (or s7), the PDopa-to-PAH molar ratio (x : y) is calculated to be 2.67 : 1. In the case of $PDopa_1$-$PAH_{3.5}$ PECs, the N 1s signals of their XPS spectra reveals that A_{PEC}^{NH} = 31.63%, A_{PEC}^{NH3} = 64.33%, and A_{PEC}^{NH2} = 4.05%. According to Equation s8 (or s7), the PDopa-to-PAH molar ratio (x : y) is calculated to be 1 : 1.51.

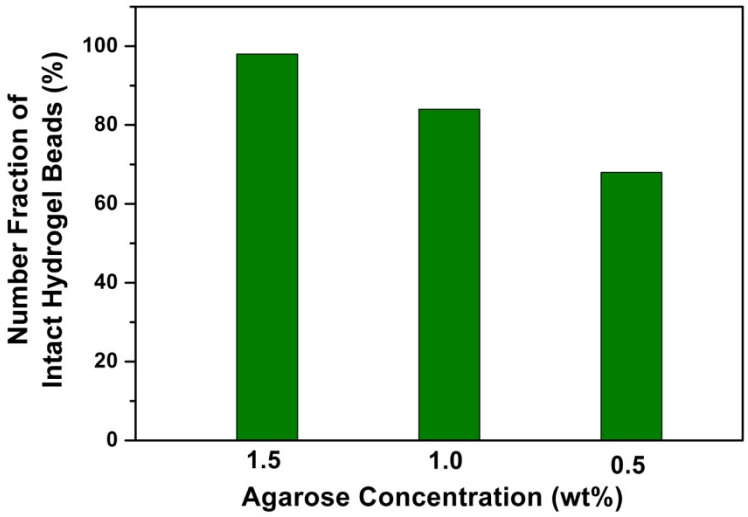


Figure S4. Plot of the number fraction of intact, spherical PDopa-PAH PEC-loaded agarose hydrogel beads after stirring at 300 rpm in water for 2 days versus the concentration of agarose (wt %) used for preparation of the hydrogel beads. The numbers of freshly prepared hydrogel beads, used for this experiment, is 200. After stirring treatment, the number of the intact hydrogel beads are counted and normalized by 200, yielding the number fractions. This figure shows that the composite hydrogel beads prepared at the agarose concentration of 1.5 wt% are much more stable compared to those prepared from agarose solutions at low agarose concentrations of 1.0 wt% and 0.5 wt%.

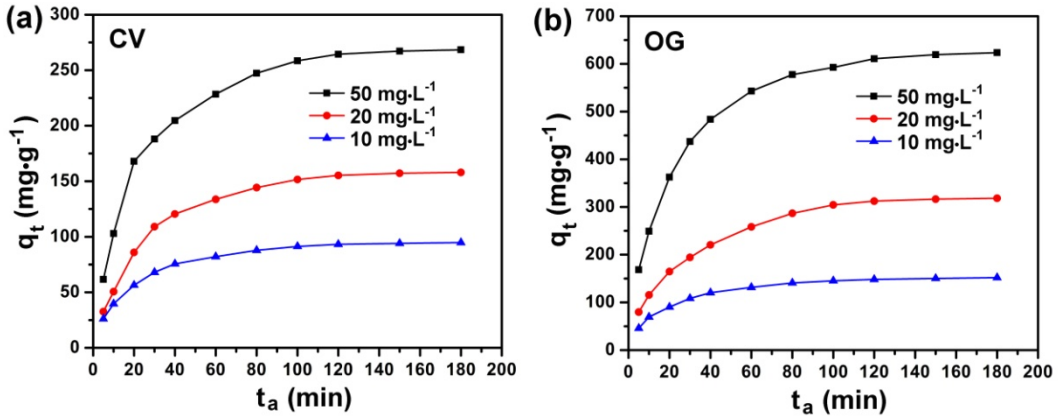


Figure S5. (a, b) The kinetics profiles of adsorption of ionic organic dyes by PDopa-PAH PECs loaded in the agarose hydrogel beads at the initial dye concentrations of 10 mg·L^{-1} (solid up triangles), 20 mg·L^{-1} (solid circles), and 50 mg·L^{-1} (solid squares). (a) CV is adsorbed by the $PDopa_{3.5}$-PAH_1 PECs and (b) OG by the $PDopa_1$-$PAH_{3.5}$ PECs.