Supporting information materials

Poly (vinyl alcohol) (PVA) enhanced hybrid hydrogels of hyperbranched poly(ether amine) (hPEA) for selective adsorption and separation of dyes

Shujun Deng, Hongjie Xu, Xuesong Jiang*, Jie Yin

School of Chemistry & Chemical Engineering, State Key Laboratory for Metal Matrix Composite Materials, Shanghai Jiao Tong University,

Shanghai 200240, People's Republic of China.

Tel.: +86-21-54743268; Fax: +86-21-54747445. E-mail: ponygle@sjtu.edu.cn

As shown in Figure S1, the peak at 1030cm^{-1} corresponding to Si-O-C groups suggests that PVA can be bonded to the crosslinked network of $SiO_{1.5}$-hPEA-Gels through the hydrolysis of trimethoxylsilane groups of TMS-hPEA and hydroxyl groups of PVA.

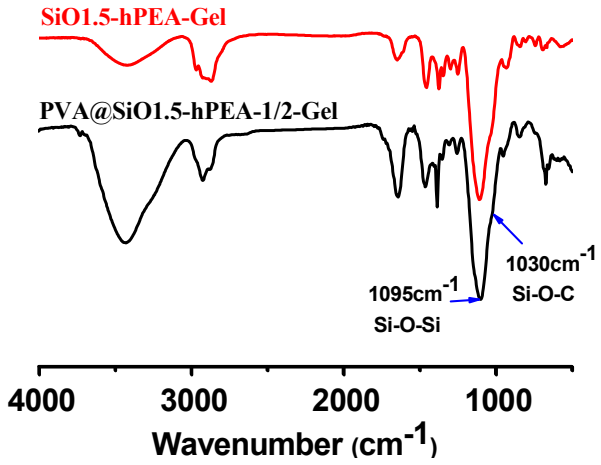


Figure S1. FT-IR of $SiO_{1.5}$-hPEA-Gels and PVA@ $SiO_{1.5}$-hPEA-Gels

The pure physical crosslinked PVA hydrogel without hPEA was prepared as for reference. As shown in Figure S2, the pure PVA hydrogel can not adsorb the

hydrophilic dyes PS and MB, indicating that PVA has on interaction with dyes in water.

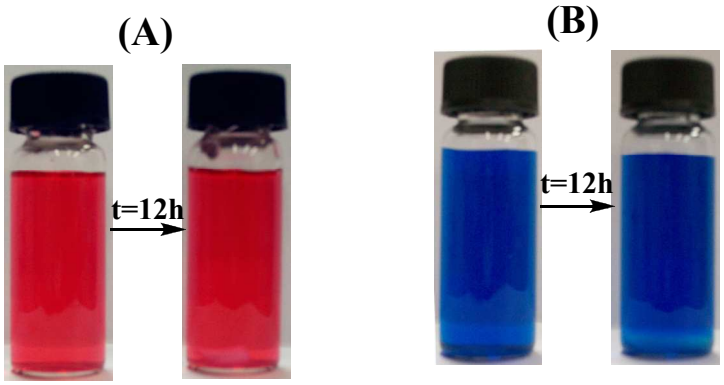


Figure S2. Photos of solution of PS (A) and MB (B) before and after adsorption by the pure PVA hydrogel.

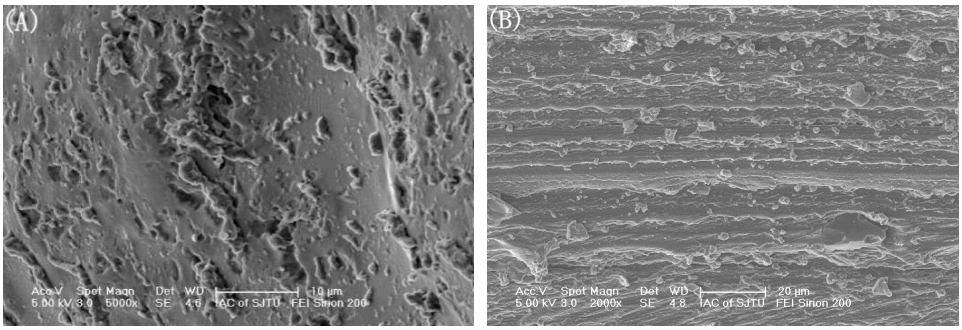


Figure S3. Representative SEM images of (A) PVA@$SiO_{1.5}$-hPEA-1/2-Gel and (B) PVA@$SiO_{1.5}$-hPEA-1/4-Gel at 25 ^{o}C.

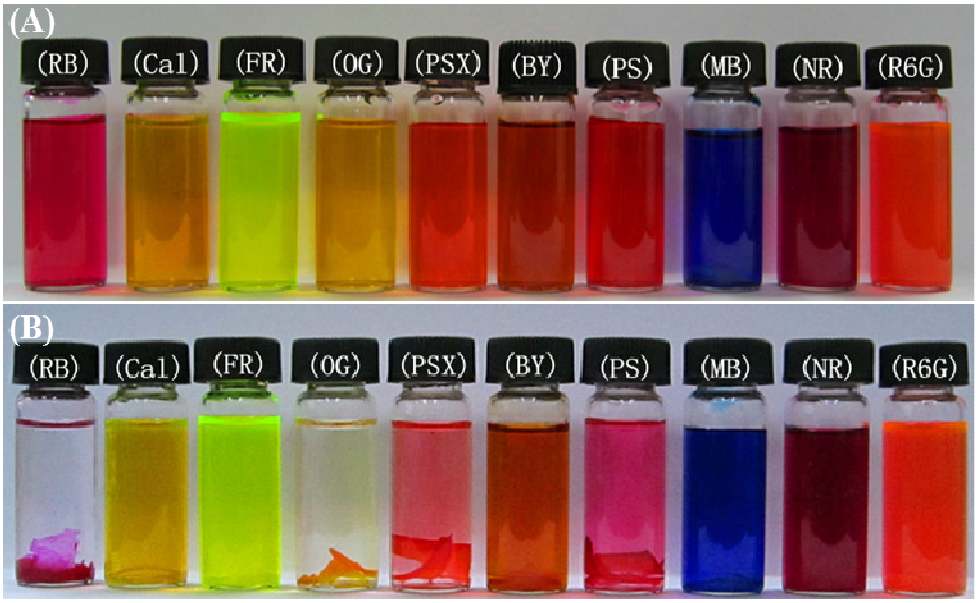
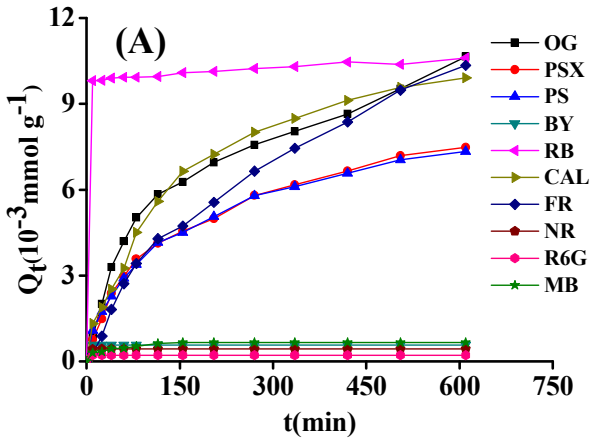


Figure S4. Photos of solution of dyes (A) before and (B) after adsorption by PVA@$SiO_{1.5}$-hPEA-1/2-Gel. Initial dye concentration is 200 μM.



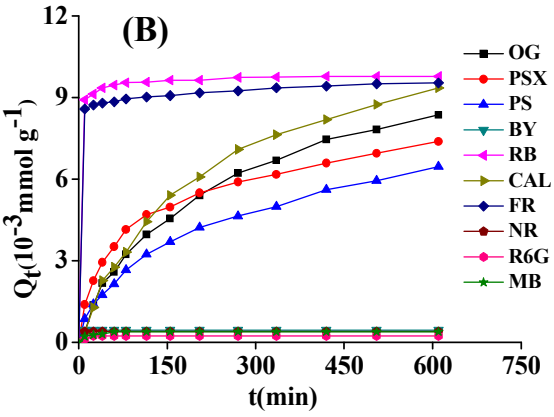


Figure S5. Adsorption capacity Q_t versus time curves for the adsorption of RB, Cal, FR, OG, PSX, PS, BY, NR, R6G and MB onto (A) PVA@$SiO_{1.5}$-hPEA-1/4-Gel, (B) PVA@$SiO_{1.5}$-hPEA-1/3-Gel, at 25 °C.

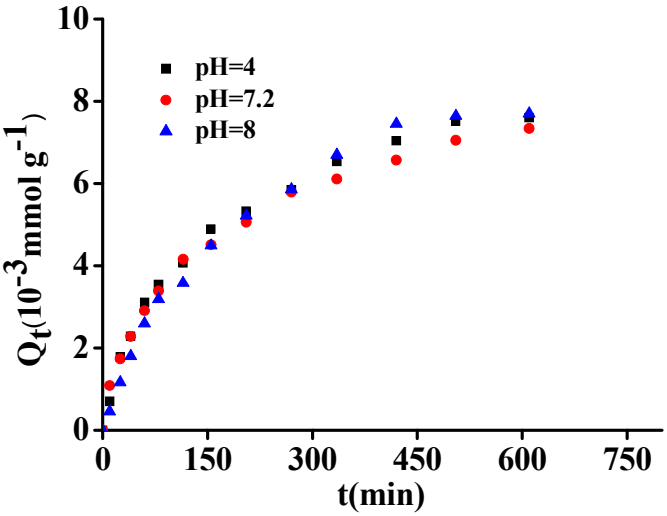
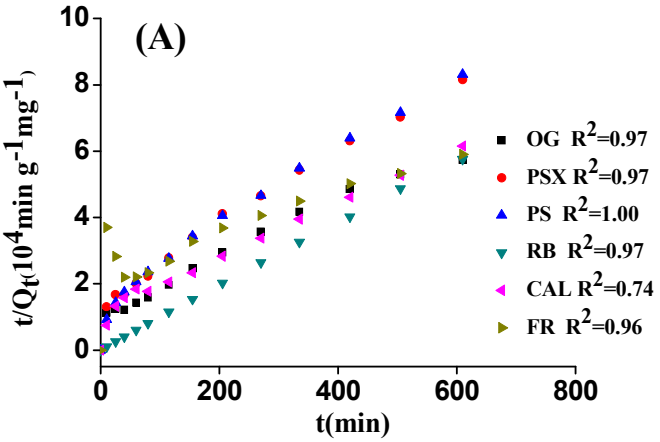


Figure S6. Effect of pH on the adsorption of PS by PVA@$SiO_{1.5}$-hPEA-1/2-Gel at 25 °C.



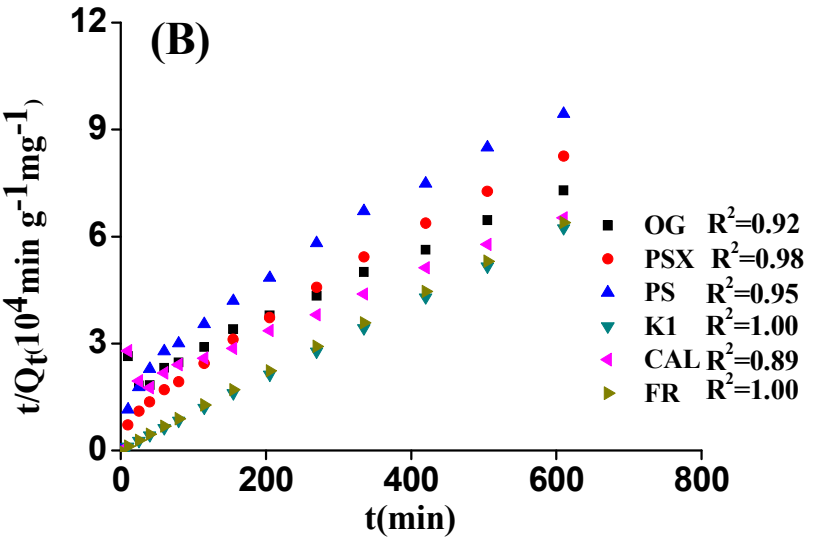


Figure S7. Pseudo-second adsorption kinetics of OG, PSX, PS, RB, CAL and FR onto (A) PVA@$SiO_{1.5}$-hPEA-1/4-Gel, (B) PVA@$SiO_{1.5}$-hPEA-1/3-Gel at 25 °C.

Table S1. Kinetics parameters describing the adsorption of dyes onto PVA@$SiO_{1.5}$-hPEA-1/4-Gel and PVA@$SiO_{1.5}$-hPEA-1/3-Gel.

	PVA@$SiO_{1.5}$-hPEA-1/4 -Gel				PVA@$SiO_{1.5}$-hPEA-1/3-Gel			
	$q_{e,exp}$ (mmol/g)	k[a] (g/mmolmin)	$q_{e,cal}$ (mmol/g)	R^2	$q_{e,exp}$ (mmol/g)	k[a] (g/mmolmin)	$q_{e,cal}$ (mmol/g)	R^2
OG	1.07E-02	8.61E-01	1.13E-02	0.960	9.83E-03	5.96E-01	1.03E-02	0.922
PSX	8.94E-03	1.20E+00	8.34E-03	0.969	7.70E-03	2.11E+00	7.69E-03	0.984
PS	8.96E-03	1.38E+00	8.06E-03	0.972	8.13E-03	1.29E+00	7.08E-03	0.954
BY	5.78E-04	-	5.78E-04	1.000	4.52E-04	-	4.52E-04	1.000
RB	1.07E-02	2.33E+01	1.05E-02	1.000	9.79E-03	5.41E+01	9.81E-03	1.000
CAL	1.11E-02	8.36E-01	1.14E-02	0.966	9.36E-03	4.46E-01	1.20E-02	0.893
FR	1.08E-02	2.25E-01	1.48E-02	0.737	9.79E-03	2.32E+01	9.55E-03	1.000
NR	4.45E-04	-	4.45E-04	1.000	3.91E-04	-	3.91E-04	1.000
R6G	2.20E-04	-	2.20E-04	1.000	2.34E-04	-	2.35E-04	1.000
MB	6.69E-04	-	6.92E-04	0.998	3.89E-04	-	3.93E-04	1.000

[a] For dyes with extremely low adsorption capacity such as BY, R6G, MB and NR, because the intercepts of plots are infinitely close to zero, k values will be infinitely close to large values and make no sense.

The equilibrium adsorption data was analyzed by using the Langmuir and Freundlich isotherm models. The form of the Langmuir isotherm is expressed as follows[1]

$$\frac{C_{\mathrm{eq}}}{Q_{eq}} = \frac{C_{eq}}{Q_{\max}} + \frac{1}{K_L Q_{\max}} \tag{1}$$

where C_{eq} (mmol/L) is the equilibrium concentration of the dyes in the solution, Q_{eq} (mmol/g) is the amount of dyes adsorbed at the equilibrium, Q_{max} (mmol/g) is the maximum capacity of the hybrid hydrogel, K_L (L/mmol) is the Langmuir adsorption constant. Unlike the Langmuir model, the Freundlich model is used to describe the adsorption of an absorbate on a heterogeneous surface of an adsorbent[3]. The linearized form of the Freundlich isotherm can be given as follows[2]

$$\ln Q_{\mathrm{eq}} = \ln K_F + b_F \ln C_{eq} \tag{2}$$

Where C_{eq} (mmol/L) is the equilibrium concentration of the dyes in the solution, Q_{eq} (mmol/g) is the amount of dyes adsorbed at the equilibrium, K_F is the Freundlich constant, and b_F is a constant for depicting the adsorption intensity.

Figure S6(A) shows the linear Langmuir isotherms for OG onto PVA@$SiO_{1.5}$-hPEA-1/2-Gel and PVA@$SiO_{1.5}$-hPEA-SA-1/2-Gel, and the corresponding correlation coefficients for adsorption of OG onto PVA@$SiO_{1.5}$-hPEA-1/2-Gel and PVA@$SiO_{1.5}$-hPEA-SA-1/2-Gel are 0.995, respectively. The high correlation coefficients indicated that the Langmuir model is suitable for describing the adsorption equilibrium of OG by the hybrid hydrogels. As shown in the linear Freundlich isotherms for MB onto PVA@$SiO_{1.5}$-hPEA-1/2-Gel and PVA@$SiO_{1.5}$-hPEA-SA-1/2-Gel (Figure S6B), the corresponding correlation coefficients are 0.996 and 1, respectively. The high correlation coefficient confirmed that the adsorption of MB obeyed the Freundlich model. The adsorption isotherm parameters are summarized in Table S2

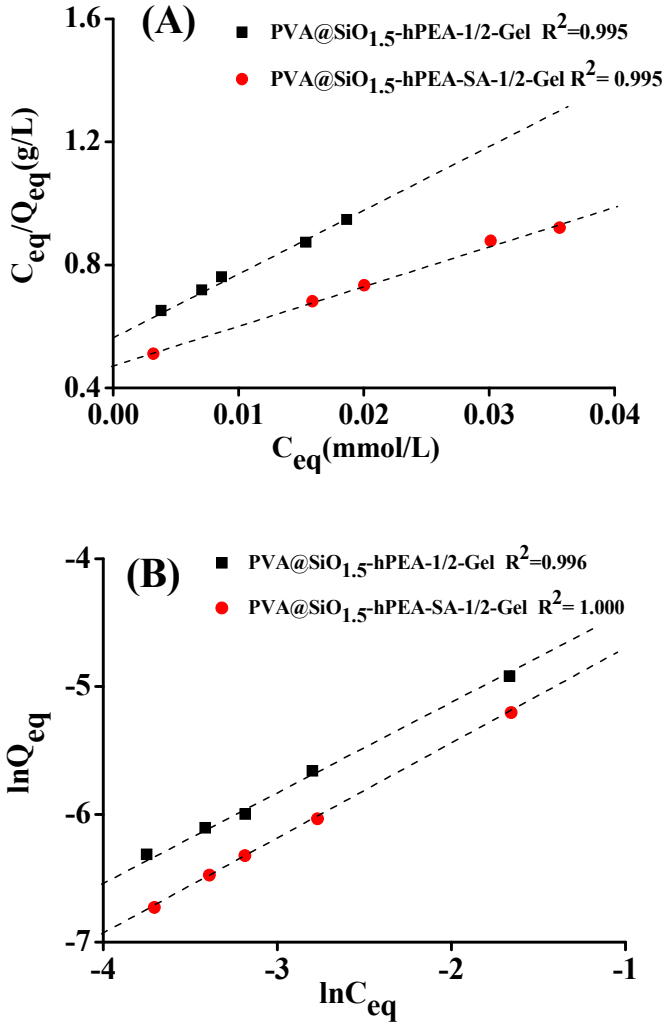


Figure S8. (A) Linearized Langmuir isotherms of OG and (B) Linearized Freundlich isotherms of MB onto PVA@$SiO_{1.5}$-hPEA-1/2-Gel and PVA@$SiO_{1.5}$-hPEA-SA-1/2-Gel at 25 ^{o}C and pH 7.2.

Table S2. Langmuir adsorption isotherm constants of OG and Freundlich adsorption isotherm constants of MB onto PVA@$SiO_{1.5}$-hPEA-1/2-Gel and PVA@$SiO_{1.5}$-hPEA-SA-1/2-Gel.

	Langmuir parameters			Freundlich parameters		
	Q_m (mmol/g)	K_L (mmol/g)	R^2	K_F	b_F	R^2
PVA@$SiO_{1.5}$-hPEA-1/2-Gel	0.051	33.4	0.995	0.023	0.679	0.996
PVA@$SiO_{1.5}$-hPEA-SA-1/2-Gel	0.078	27.2	0.995	0.019	0.738	1.000

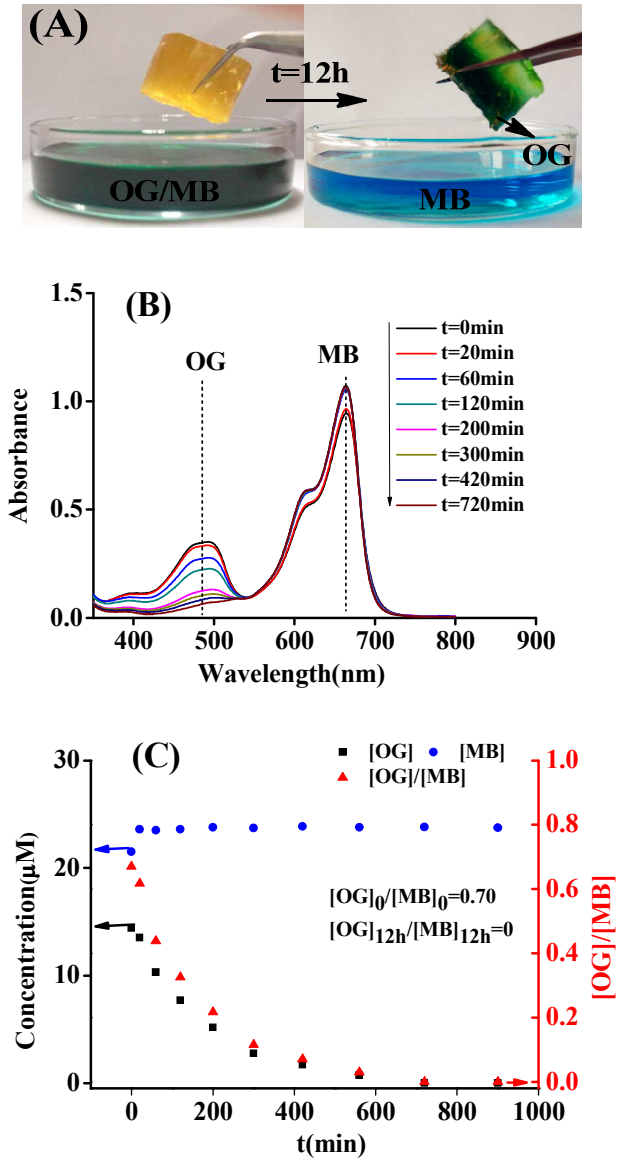


Figure S9. One-pot separation of mixed dyes OG-MB in aqueous solution. Photograph of OG-MB (A) before and after separation for 12 h by using PVA@$SiO_{1.5}$-hPEA-1/2-Gel at 25 ^{o}C. UV-vis spectra of OG-MB (B) during separation experiment. (C) Dye concentration of [OG], [MB] and dye concentration ratio of the mixed dyes in solution ([OG]/[MB]) after separation by using PVA@$SiO_{1.5}$-hPEA-1/2-Gel. Comparison of [OG] (■) and [MB] (●) with [OG]/[MB] (▲). Concentration of PVA@$SiO_{1.5}$-hPEA-1/2-Gel in solution was fixed as 2g/L.

References:

1. Langmiur, I. J. *Am. Chem. Soc.* 1916, 38, 2221-2295
2. Freundlich, H. M. F. *Phys. Chem.* 1906, 57, 385