

Electronic Supplementary Information

**Selective adsorption and separation of organic dyes from aqueous solution on  
organic-inorganic hybrid cyclomatrix polyphosphazene submicro-spheres**

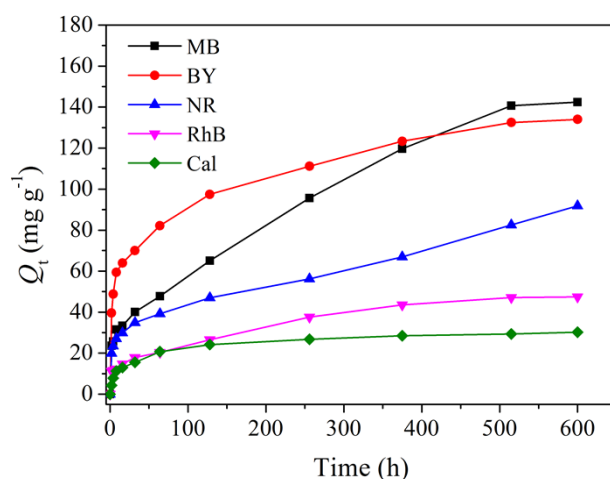
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## 1. Adsorption kinetics

The adsorption kinetic experiments were performed by stirring 10 mg of PZS submicro-spheres together with 50 mL of the aqueous solution of dye at 25 °C in darkness for different time (0-600 h). The initial concentrations of Cal, RhB, BY, MB, and NR were 0.026, 0.031, 0.101, 0.100, and 0.083 mmol L<sup>-1</sup>, respectively. At given time intervals, the concentration of dye in solution was measured by UV-visible spectra to calculate the adsorbed amount of dye on PZS submicro-spheres.



**Fig. S1** Curves of adsorption capacity  $Q_t$  versus time for the adsorption of MB, BY, NR, RhB, and Cal by PZS submicro-spheres at 25 °C. 10 mg of the submicro-spheres was added into 50 mL of the aqueous solution of dye, and the initial concentrations of MB, BY, NR, RhB, and Cal were 0.100, 0.101, 0.083, 0.031, and 0.026 mmol L<sup>-1</sup>, respectively.

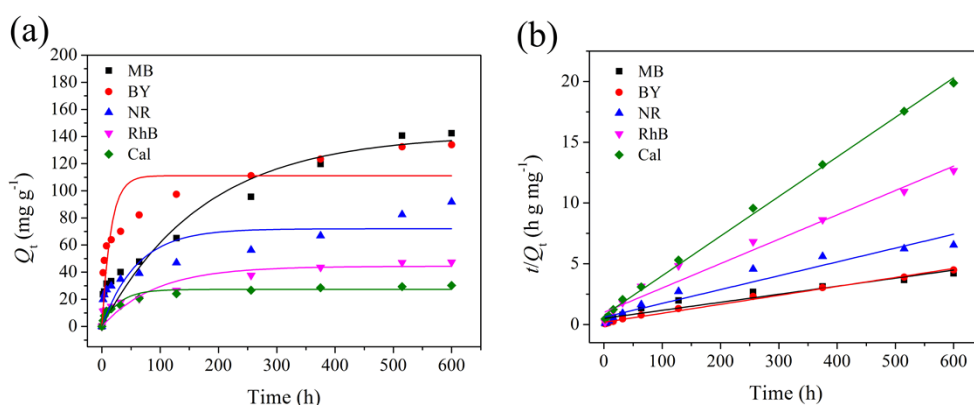
The effects of contact time on the adsorption capacities of PZS submicro-spheres towards MB, BY, NR, RhB, and Cal are shown in Fig. S1. For the five dyes, it can be seen that the adsorption capacity increases rapidly in 30 h and then continues to increase with the contact time at a relatively slow rate. After 600 h, the adsorption

equilibrium is observed for MB, BY, RhB, and Cal. For NR, however, an increase of adsorption capacity with time is still exhibited. The pseudo-first-order and pseudo-second-order kinetic models were employed to further investigate the adsorption kinetics of dyes onto PZS submicro-spheres, which are expressed in an exponential form as Eq. S1 and a linear form as Eq. S2, respectively, as follows:<sup>1</sup>

$$Q_t = Q_{eq}(1 - e^{-k_1 t}) \quad (S1)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_{eq}^2} + \frac{t}{Q_{eq}} \quad (S2)$$

where  $Q_t$  and  $Q_{eq}$  ( $\text{mg g}^{-1}$ ) are the amount of the dyes adsorbed per gram of PZS submicro-spheres at time  $t$  (h) and equilibrium, respectively,  $k_1$  ( $\text{h}^{-1}$ ) and  $k_2$  ( $\text{g mg}^{-1} \text{h}^{-1}$ ) are the pseudo-first-order rate constant and pseudo-second-order rate constant, respectively. The curve-fitting plots of the pseudo-first-order kinetics and pseudo-second-order kinetics are shown in Fig. S2a and b, respectively. The parameters  $k_1$ ,  $k_2$ , correlation coefficient ( $R^2$ ), and the calculated  $Q_{eq}$  for the two models are determined and summarized in Table S1. Obviously, for all the five dyes,



**Fig. S2** Fitting curves of the pseudo-first-order kinetic model (a) and pseudo-second-order kinetic model (b) for the adsorption of MB, BY, NR, RhB, and Cal by PZS submicro-spheres at 25 °C.

**Table S1** Kinetic parameters for the adsorption of MB, BY, NR, RhB, and Cal onto PZS submicro-spheres<sup>a</sup>

	Pseudo-first order				Pseudo-second order		
	$Q_{eq,exp}$ (mg g <sup>-1</sup> )	$k_1$ (10 <sup>-3</sup> h <sup>-1</sup> )	$Q_{eq,cal}$ (mg g <sup>-1</sup> )	$R^2$	$k_2$ (10 <sup>-4</sup> g mg <sup>-1</sup> h <sup>-1</sup> )	$Q_{eq,cal}$ (mg g <sup>-1</sup> )	$R^2$
MB	142.46	5.73	141.52	0.8868	0.87	151.29	0.9327
BY	133.99	66.06	111.15	0.7472	2.93	135.59	0.9920
NR	116.73	16.76	71.99	0.6870	2.16	87.95	0.9382
RhB	47.37	10.87	44.36	0.8300	4.06	49.83	0.9743
Cal	30.20	34.78	27.31	0.9176	13.92	30.70	0.9977

<sup>a</sup> The concentration of PZS submicro-spheres in the aqueous solutions of dyes (50 mL) is 0.2 g L<sup>-1</sup>.

The initial concentrations of MB, BY, NR, RhB, and Cal in aqueous solutions are 0.100, 0.101, 0.083, 0.031, and 0.026 mmol L<sup>-1</sup>, respectively.

the pseudo-second-order kinetic model fits better to the whole range of the contact time than the pseudo-first-order one. The correlation coefficients of the pseudo-second-order fitting are much higher than that of the pseudo-first-order one. In addition, the  $Q_{eq}$  values obtained by experiments ( $Q_{eq,exp}$ ) are approximately equal to the calculated values ( $Q_{eq,cal}$ ) based on the pseudo-second-order model. Therefore, the adsorption kinetics of dyes by PZS submicro-spheres can be better described by the pseudo-second-order kinetic model rather than the pseudo-first-order one.

## 2. Isotherm study

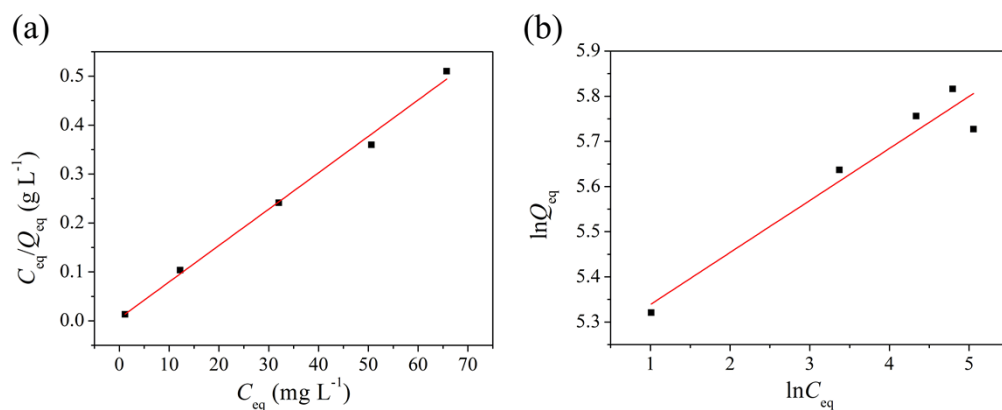
As is well-known, equilibrium adsorption isotherm is useful to study the interaction of adsorbent with dye and estimate the characteristics of adsorption system by providing the relationship between the concentration of the dye in solution and the amount of the dye adsorbed onto the adsorbent when the adsorption equilibrium is reached. BY was chosen as a representative dye to study the isotherm. A batch of BY aqueous solutions with different initial concentrations (0.023, 0.057, 0.108, 0.155 and 0.188 mmol L<sup>-1</sup>) were prepared. In each solution (100 mL), 10 mg of PZS submicro-spheres was added. The suspension was oscillated at 25 °C in darkness to reach adsorption equilibrium, and then the final concentration of dye in the solution and the equilibrium adsorption capacity of the adsorbent was analyzed according to the UV-visible spectrophotometry.

The equilibrium adsorption data was fitted to the Langmuir and Freundlich models expressed in the linear forms as Eqs. S3 and S4, respectively, as follows:

$$\frac{C_{\text{eq}}}{Q_{\text{eq}}} = \frac{1}{K_L Q_{\text{max}}} + \frac{C_{\text{eq}}}{Q_{\text{max}}} \quad (\text{S3})$$

$$\ln Q_{\text{eq}} = \ln K_F + b_F \ln C_{\text{eq}} \quad (\text{S4})$$

where  $C_{\text{eq}}$  (mg L<sup>-1</sup>) and  $Q_{\text{eq}}$  (mg g<sup>-1</sup>) are the concentration of the dye in solution and the amount of the dye adsorbed on PZS submicro-spheres at adsorption equilibrium, respectively,  $Q_{\text{max}}$  (mg g<sup>-1</sup>) is the theoretical monolayer saturated adsorption capacity of PZS submicro-spheres,  $K_L$  (L mg<sup>-1</sup>) is the Langmuir constant,  $K_F$  is the Freundlich constant, and  $b_F$  is a constant indicating the intensity of adsorption. Fig. S3a and b



**Fig. S3** Linear forms of the isotherms for BY adsorption by PZS submicro-spheres: Langmuir model (a) and Freundlich model (b).

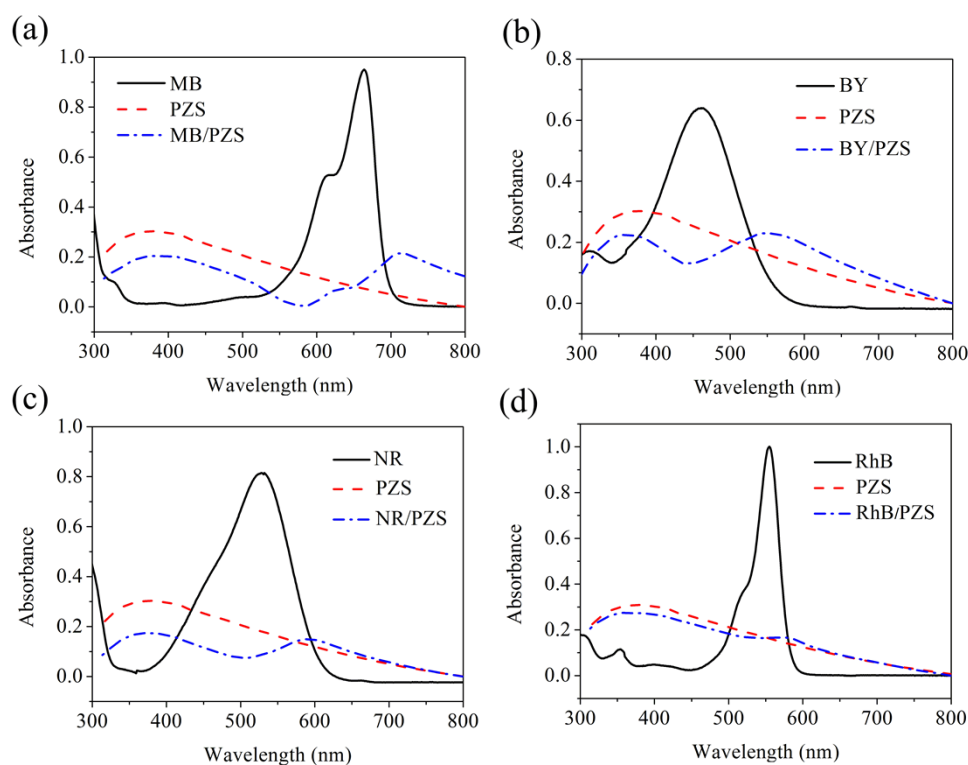
show the Langmuir and Freundlich adsorption isotherms for BY at 25 °C, respectively. The results obtained from the isotherms are given in Table S2. By comparing the correlation coefficient ( $R^2$ ) of Langmuir isotherm with that of Freundlich isotherm, it is found that the Langmuir model is more suitable for describing the adsorption behavior than the Freundlich model. Moreover, the equilibrium adsorption capacity obtained by experiment (133.99 mg g<sup>-1</sup>) is well in accord with the theoretical monolayer saturated adsorption capacity determined from the Langmuir isotherm (134.41 mg g<sup>-1</sup>). It indicates that the chemisorption dominates the adsorption of BY on PZS submicro-spheres by some interaction between the adsorbent and the dye.

**Table S2** Summary of the isotherm constants and correlation coefficients of Langmuir model and Freundlich model

Dye	Langmuir model			Freundlich model		
	$Q_{max}$ (mg g <sup>-1</sup> )	$K_L$ (L mg <sup>-1</sup> )	$R^2$	$K_F^a$	$b_F$	$R^2$
BY	134.41	1.4198	0.9932	185.59	0.1152	0.9137

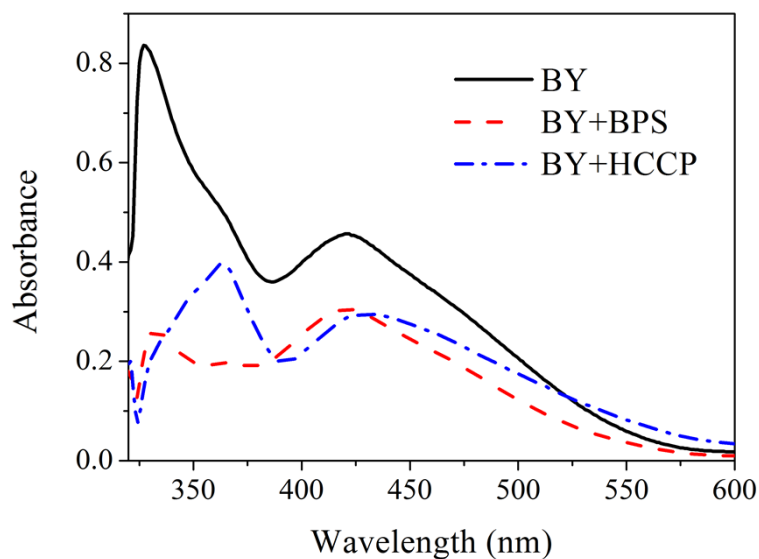
<sup>a</sup> The unit for the  $K_F$  is “mg<sup>1-1/n</sup>L<sup>1/n</sup>g<sup>-1</sup>”.

### 3. Adsorption mechanism



**Fig. S4** UV-visible absorbance spectra of dyes, PZS submicro-spheres, and the PZS submicro-spheres after adsorption of the dyes in aqueous solution. (a) MB, (b) BY, (c) NR, and (d) RhB.

The UV-visible absorbance spectra of dyes (MB, BY, NR, and RhB), PZS submicro-spheres, and the submicro-spheres with an adsorption of the dyes in aqueous solution were recorded, as shown in Fig. S4. It is clear that after adsorption by PZS submicro-spheres, the characteristic absorption peaks of the four dyes all exhibit bathochromic shift, indicating the existence of some host-guest interaction between PZS submicro-spheres and the dyes. This result also prove that the chemisorption plays a dominant role in this study.



**Fig. S5** UV-visible absorbance spectra of BY in acetone, the mixture of BY and BPS in acetone, and the mixture of BY and HCCP in acetone.

To evaluate the contribution of nitrogen atoms and oxygen atoms to the construction of the acid-base interaction, we employed BY as a representative dye, and investigated its possible interactions with the two monomers HCCP and BPS by UV-visible spectrophotometry. Considering the reactivity of HCCP in water, acetone was chosen as medium, and the UV-visible absorption spectra of BY in acetone, the mixture of BY and BPS in acetone, and the mixture of BY and HCCP in acetone were recorded. It can be speculated that if there is some interaction between the dye and the monomer, a change of the characteristic absorption peak of the dye in position should be observed in the UV-visible absorption spectrum of the mixture. The results are shown in Fig. S5. It is obvious that the addition of HCCP into the acetone solution of BY can make the characteristic absorption peak of BY shift bathochromically. However, no change of the characteristic absorption peak of BY in position is observed after the addition of BPS. This result demonstrates that, for our system, the nitrogen atoms play



an important part in establishing the acid-base interaction, but the oxygen atoms (O=S=O) exhibit a negligible effect. It is possible that the electron-donating or proton-attracting ability (i.e. alkalinity) of nitrogen atoms in PZS towards the dyes is much stronger than that of the oxygen atoms (O=S=O).

## References

- 1 L. H. Ai, C. Y. Zhang, F. Liao, Y. Wang, M. Li, L. Y. Meng and J. Jiang, *J. Hazard. Mater.*, 2011, **198**, 282-290.