Supplementary Material (ESI)

Supporting Information

Hypervalent silicon-based, anionic porous organic polymers with solid microsphere or hollow nanotube morphologies and exceptional capacity for selective adsorption of cationic dyes

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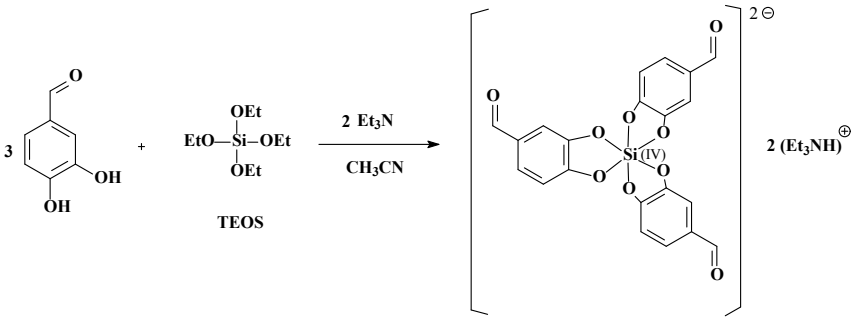
1. Experimental section

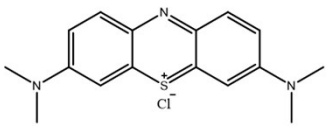
1.1 Synthesis of the Si-precursor



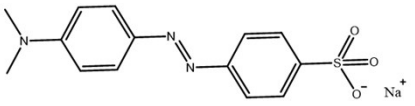
Si-precursor

The Si-precursor $(Et_3NH)_2\{[(CHO)C_6H_3O_2]_3Si\}$ was prepared following a slightly modified literature procedure resulting in increased isolated yields[1]. 3,4-Dihydroxybenzaldehyde (10.0 g, 72.5 mmol) and triethylamine (4.5 g, 48.5 mmol) were stirred at room temperature in acetonitrile (125 mL) then a solution of TEOS (5.05g, 24 mmol) in acetonitrile (50 mL) was added dropwise, over a period of about 1 hour. After 24h the solution was concentrated to dryness by rotary

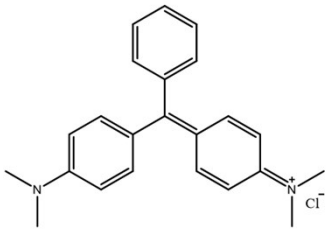
evaporation, washed with ether and dried to give 12.59 g (94%) of Si-precursor. ^{1}H NMR ($CDCl_3$): δ = 1.31 (t, J = 6.9 Hz, 18H, CH_3), 3.34 (q, J = 7 Hz, 12H, CH_2), 6.5-7.2 (m, 9H, arom-H), 9.65 (s, 3H); IR(KBr): ν = 1667, 1591, 1494, 1448, 1354, 1280, 1157, 1116, 1034, 968, 836, 774, 694 cm^{-1}.



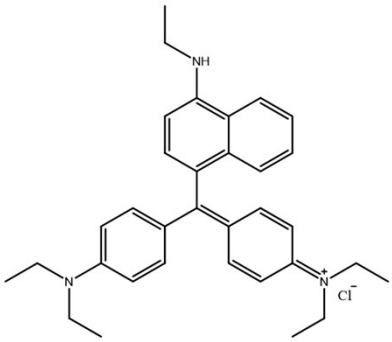
Methylene blue (MB)
Size: 17.286Å × 8.190 Å × 4.110Å



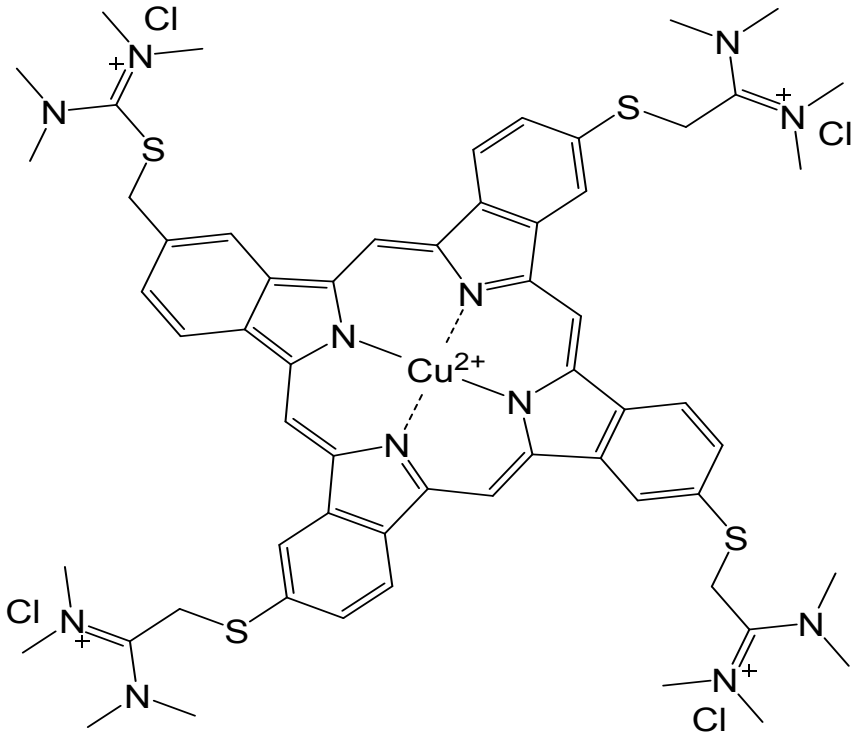
Methyl orange (MO)
Size: 18.170Å × 7.610Å ×5 .742Å



Malachite green (MG)
Size: 16.768Å × 13.112Å × 4.542Å



Basic Blue 7 (BB7)
Size: 17.651Å × 15.004Å × 8.575Å



Alcian Blue 8GX (AB8GX)
Size: 26.053Å×25.151Å×7.641Å

Figure S1 Chemical structures and molecular size of Methylene blue (MB), Malachite green (MG), Methyl orange (MO), Basic blue 7 (BB7) and Alcian Blue 8GX (AB8GX).

1.2 Kinetics adsorption experiments

Exact amounts of adsorbent Si-POP-1 (10 mg each) were put into two 150 mL beakers to which 80 mg/L MB and MG solutions were added, respectively. The bakers were placed in a thermostatic shaker bath operating below 298.15K. At the end of predetermined time intervals, the residual dye concentration in the supernatant was determined using a UV-Vis spectrophotometer at its maximum adsorption wavelength of 664 nm for MB and 615 nm for MG. For absorbent Si-POP-2, similar procedures were carried out following the above experimental conditions except that the initial dye concentrations were changed to 550 mg/L for MB and 120 mg/L for MG. The concentration of the dye retained in the adsorbent phase at time *t* was calculated using the equation of $q_t=(c_0-c_t)V/m$, where c_0 and c_t are the initial and the concentration at time *t* (mg/L) of the dye solution, V is the volume of the solution (L) and m is the mass of the adsorbent (g).

1.3 Thermodynamics adsorption experiments

0.01g Si-POP-1 were added to 50 mL MG and MB aqueous solutions with initial concentrations of 20 mg/L, 40 mg/L, 50 mg/L, 60 mg/L, 70 mg/L, 80 mg/L, 90 mg/L, 100 mg/L, 110 mg/L, 120 mg/L, 130 mg/L and 140 mg/L, respectively. The adsorption procedures were carried out in a thermostatic shaker bath at 298.15K, 303.15K and 308.15K. The effect of the initial concentration and the adsorption thermodynamics of MB on Si-POP-2 were carried out under the above conditions, while for the adsorption of MG on Si-POP-2 the initial concentrations were changed to 200 mg/L, 250 mg/L, 300 mg/L, 350 mg/L, 400 mg/L, 450 mg/L, 500 mg/L, 550 mg/L, 600 mg/L, 650 mg/L, 700 mg/L, 750 mg/L and 800 mg/L, and the initial volume to 75 mL. The concentrations of the dye retained in the adsorbent phase at equilibrium were calculated using the equation of $q_e=(c_0-c_e)V/m$, where c_0 and c_e are the initial and the equilibrium concentrations (mg/L) of the dye solution, V is the volume of the solution (L) and m is the mass of the adsorbent (g).

1.4 Effect of the ionic strength on the dye adsorption

To explore the effect of ionic strength on the dye adsorption, solutions of NaCl and $CaCl_2$ were employed with concentrations fixed at 100 mg of each salt/g adsorbent. For Si-POP-1, 25mL of the above NaCl or $CaCl_2$ solutions were added to 25mL of aqueous solution containing either 200 mg/L MB or MG.

The same procedure was repeated for Si-POP-2 except that 37.5 mL of the above NaCl or $CaCl_2$ solutions were added to 37.5 mL of aqueous solution containing either 240 mg/L MG or to a 37.5 mL solution of 1000 mg/L MB.

In all experiments the amount of adsorbent was fixed to 10 mg and the adsorption procedures were conducted at 298.15 K. Finally, the amounts of MB and MG adsorbed on Si-POP-1 and on Si-POP-2 were calculated by measuring the UV-vis spectra.

1.5 Effect of pH on the dye adsorption

To determine the adsorption capacity at pH varying from 3 to 8, 0.1 M HCl or 0.1 M NaOH aqueous solutions were used to adjust the pH. At 298.15 K, 10 mg Si-POP-1 were added to 200 mL solution containing 25 mg/L either MB or MG. In addition, 10 mg Si-POP-2 were used to absorb the dye from 200 mL of a solution containing 200 mg/L MB or 25mg/L MG, at 298.15 K.

1.6 Competitive dye adsorption experiments

To investigate the competitive adsorption of dyes with different molecular size, changes in the dye concentrations were monitored by UV-vis spectra. First, 10 mg Si-POP-1 (in a subsequent experiment Si-POP-2) were introduced, at 298.15 K, into a mixture 50 mL aqueous solution of 50 mg/L cationic MG and 50mL aqueous solution of anionic 50mg/L methyl orange (MO) and adsorption followed by UV-vis (Figure 8). Furthermore, 10 mg Si-POP-1 were put into the mixture of 50mL aqueous solution containing 80 mg/L MG and 50mL aqueous solution containing 80mg/L MB; next, 10 mg Si-POP-2 were put into the mixture of 50 mL aqueous solution containing 200 mg/L MG and 50 mL aqueous solution containing 200 mg/L MB. Adsorption was followed by UV-vis spectra (Figure 9).

1.7 Regeneration of Si-POP-2

A saturated NaCl methanol solution was added to the MB-loaded Si-POP-2, the mixture was sonicated for 30 min., and then the liquid phase was separated by centrifugation. The desorption process was repeated at least three times until no dye could be detected. Finally, Si-POP-2 was dried in a hot oven at 60°C for being used in a next run.

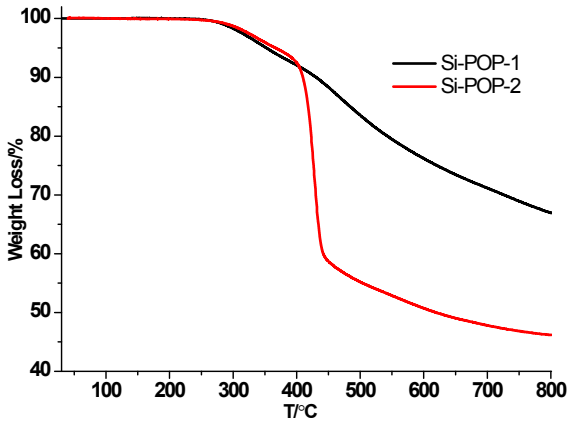


Figure S2 TGA curves of Si-POP-1 and Si-POP-2.

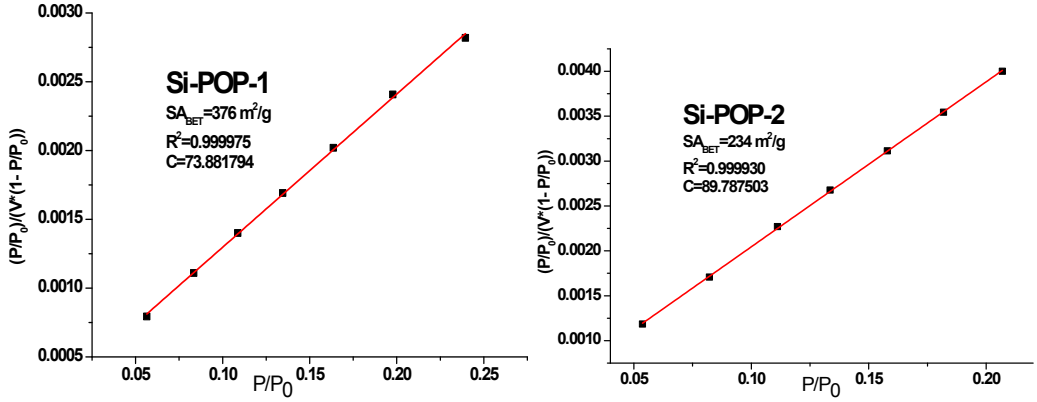


Figure S3 BET plots for Si-POP-1 and Si-POP-2 calculated from the N_2 adsorption isotherm at 77 K. The model was applied from P/P_o= 0.05-0.25.

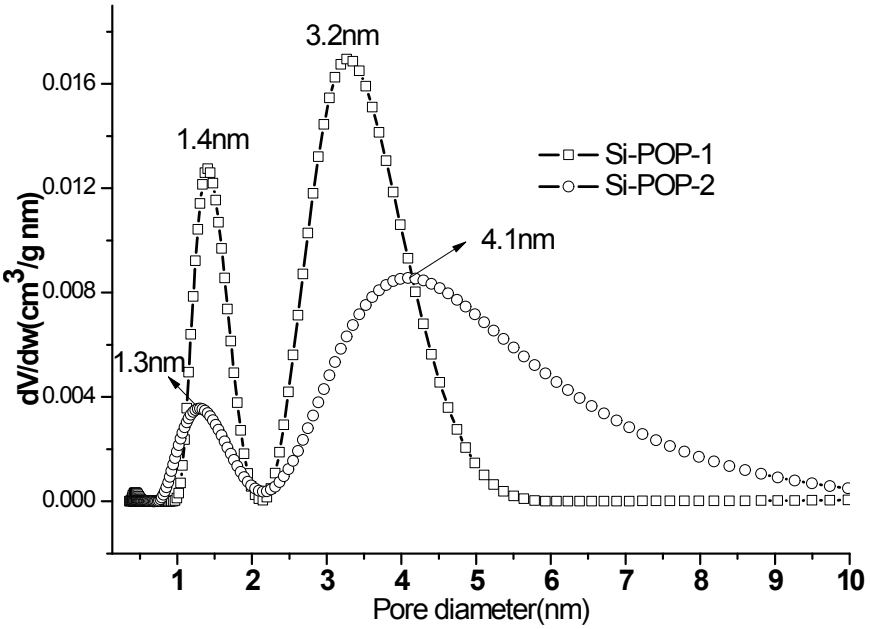


Figure S4 The pore size and pore volume fitting curves for Si-POP-1 and Si-POP-2 using the non-local density function theory (NLDFT) method.

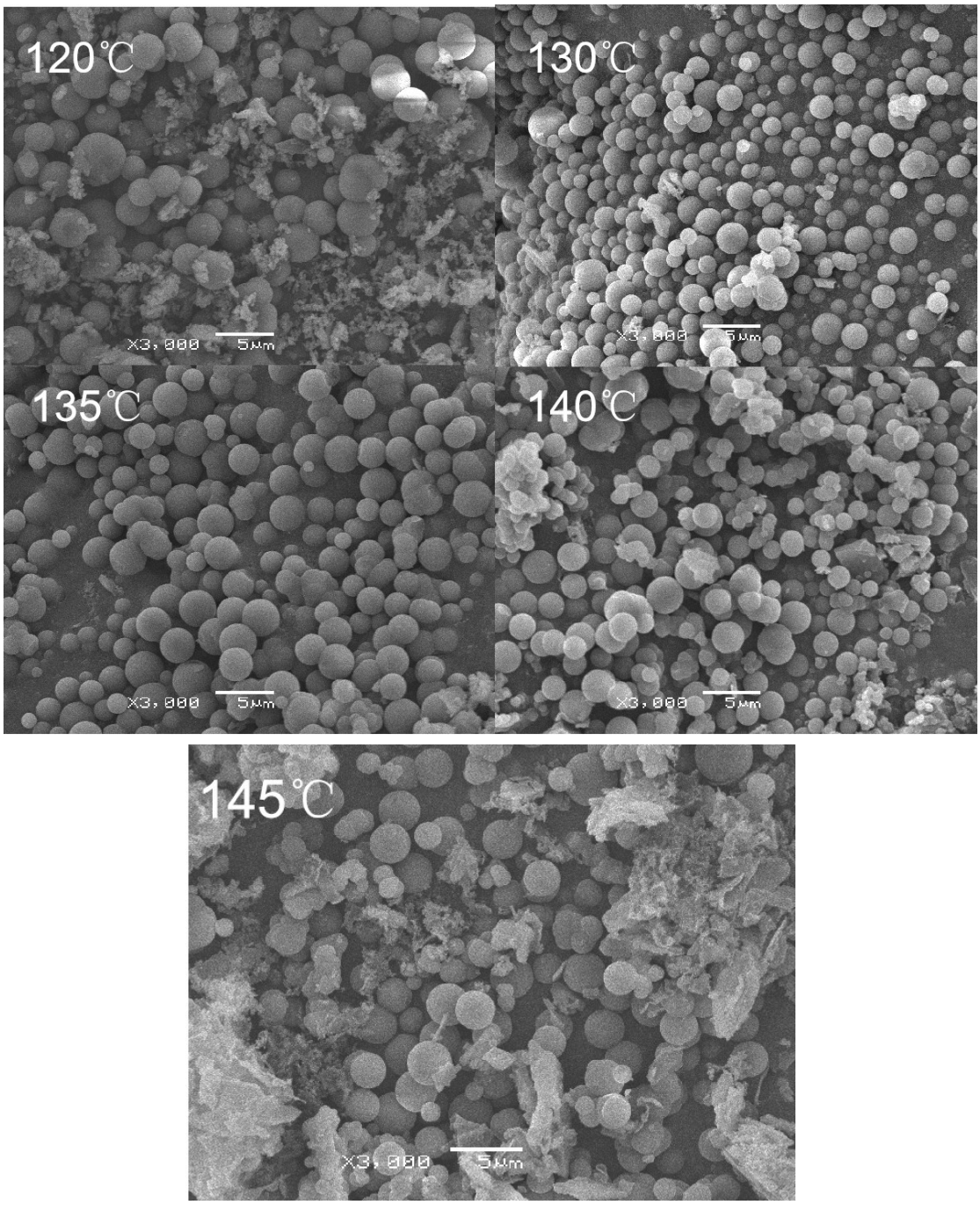


Figure S5 SEM of Si-POP-1 obtained at different temperatures.

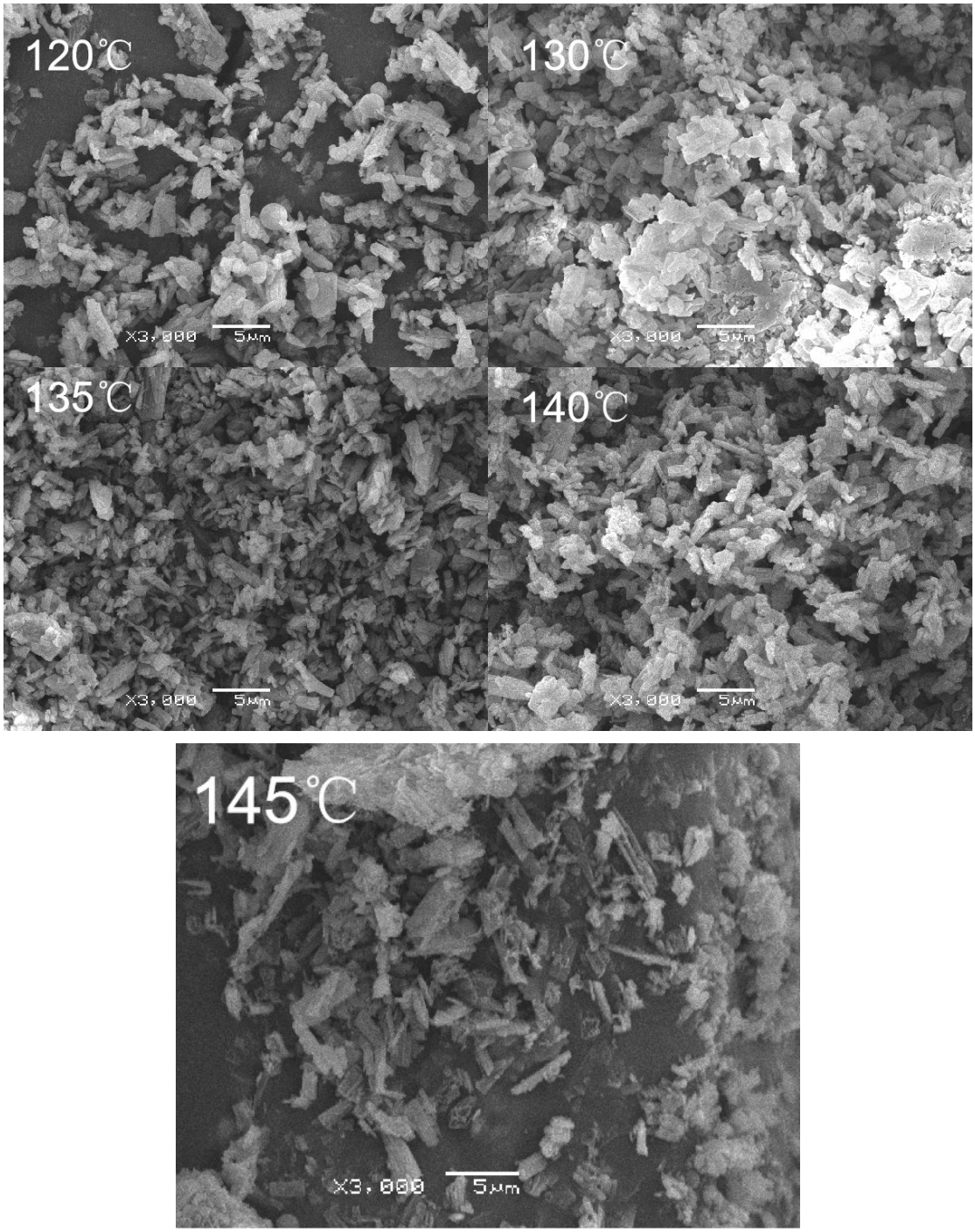


Figure S6 SEM of Si-POP-2 obtained at different temperatures.

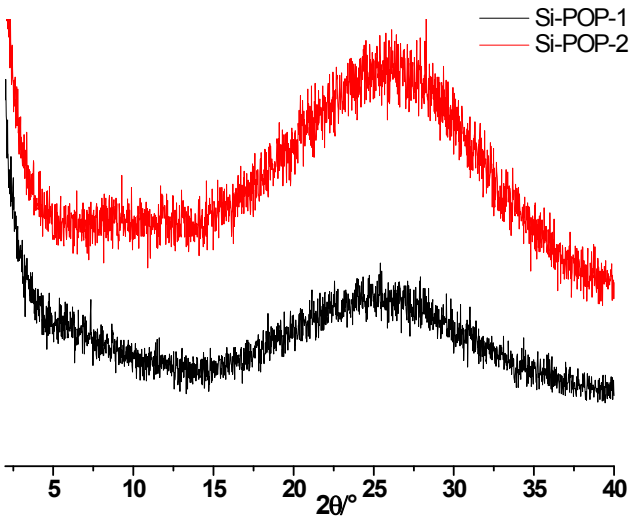


Figure S7 PXRD patterns of Si-POP-1 and Si-POP-2.

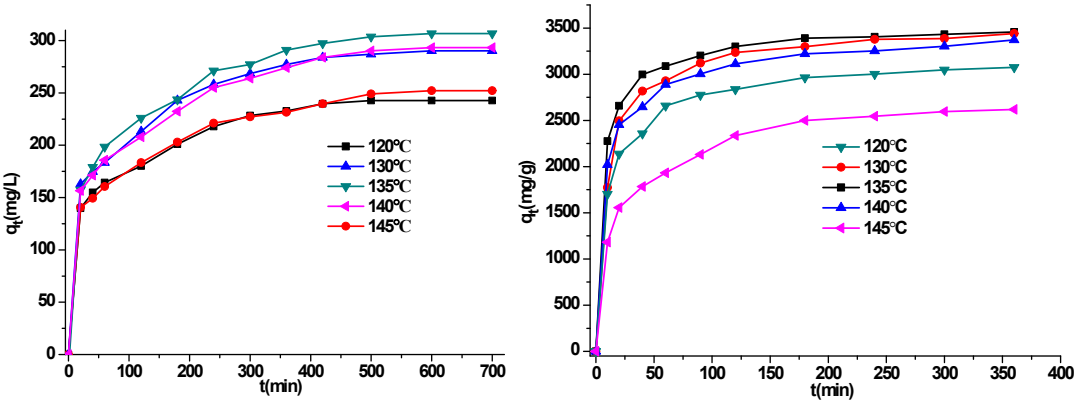


Figure S8 Adsorption capacity for MB of Si-POP-1 (left) and Si-POP-2 (right) synthesized at different temperatures. Initial volume and concentration of the dye solution: for Si-POP-1: 150 mL, 80 mg/L MB; for Si-POP-2: 150mL, 550 mg/L MB. The mass of each adsorbent, Si-POP-1 or Si-POP-2, was 20 mg.

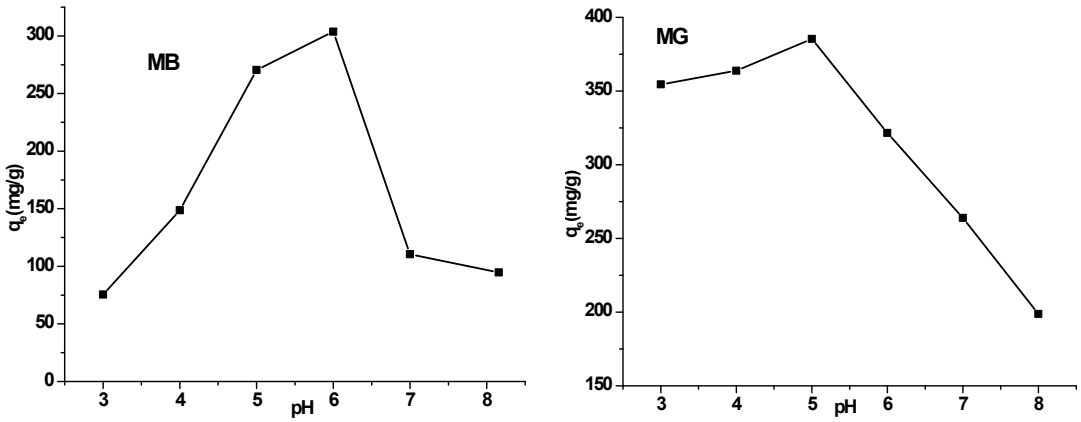


Figure S9 Effect of pH on the adsorption capacity of Si-POP-1 for MB and MG, at 25 °C.

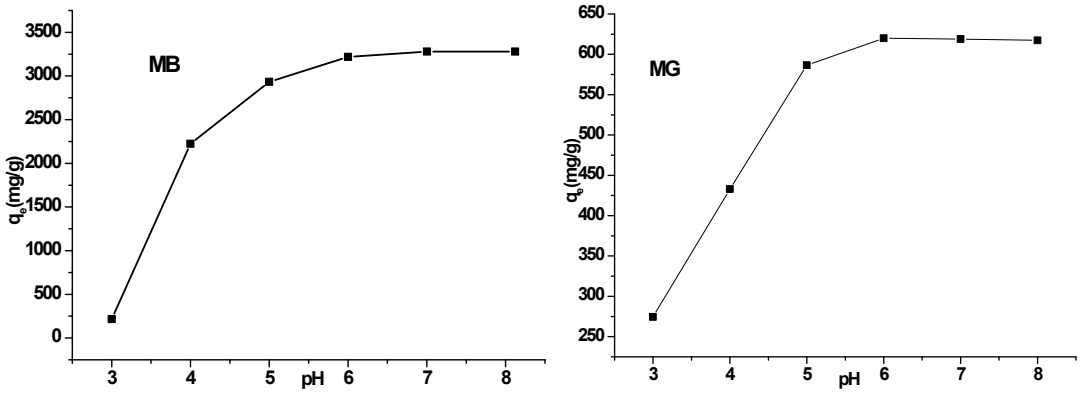


Figure S10 Effect of pH on the adsorption capacity of MB and MG on Si-POP-2, at 25 °C.

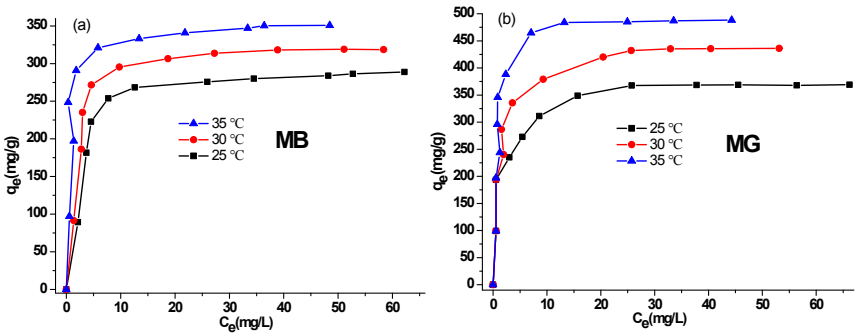


Figure S11 Equilibrium adsorption isotherms of MB (a) and MG (b) on the Si-POP-1.

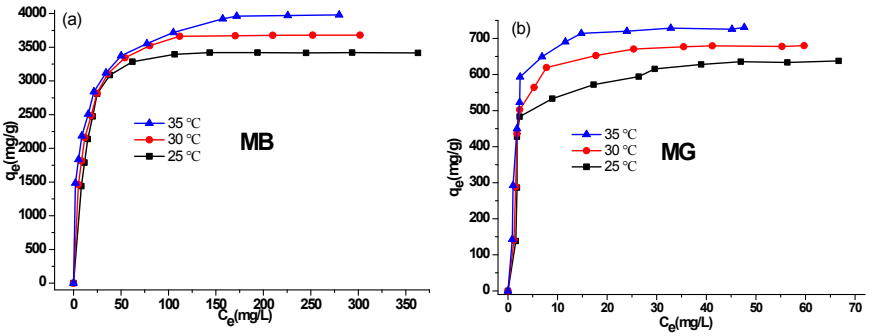
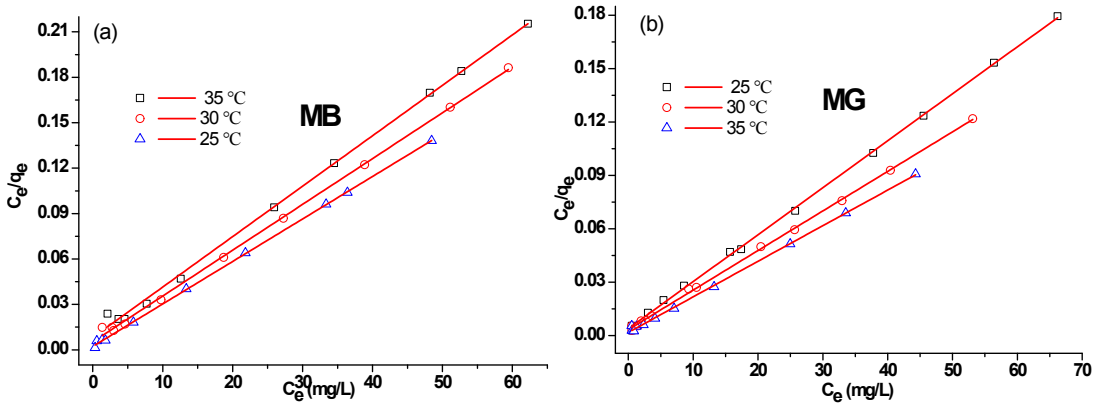


Figure S12 Equilibrium adsorption isotherms of MB (a) and MG (b) on the Si-POP-2.



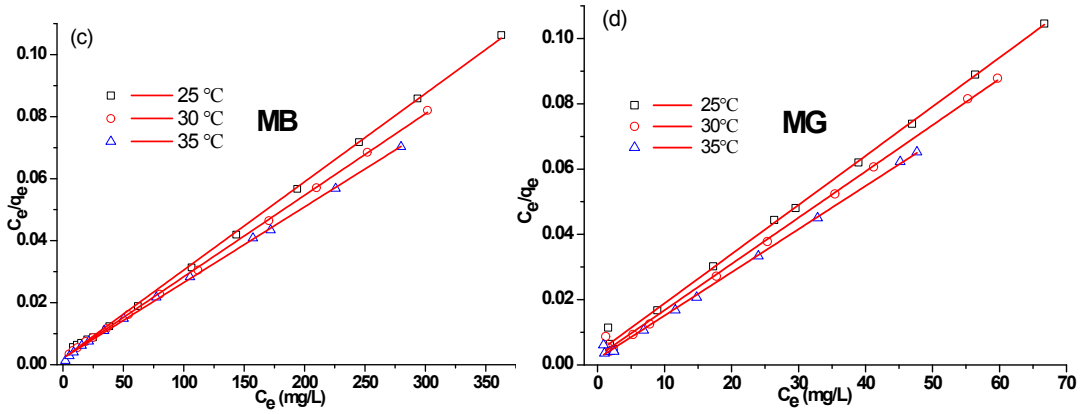


Figure S13 Linear regression of dyes adsorption by fitting the equilibrium adsorption data with the with the Langmuir model (upper figures: Si-POP-1; lower figures: Si-POP-2).

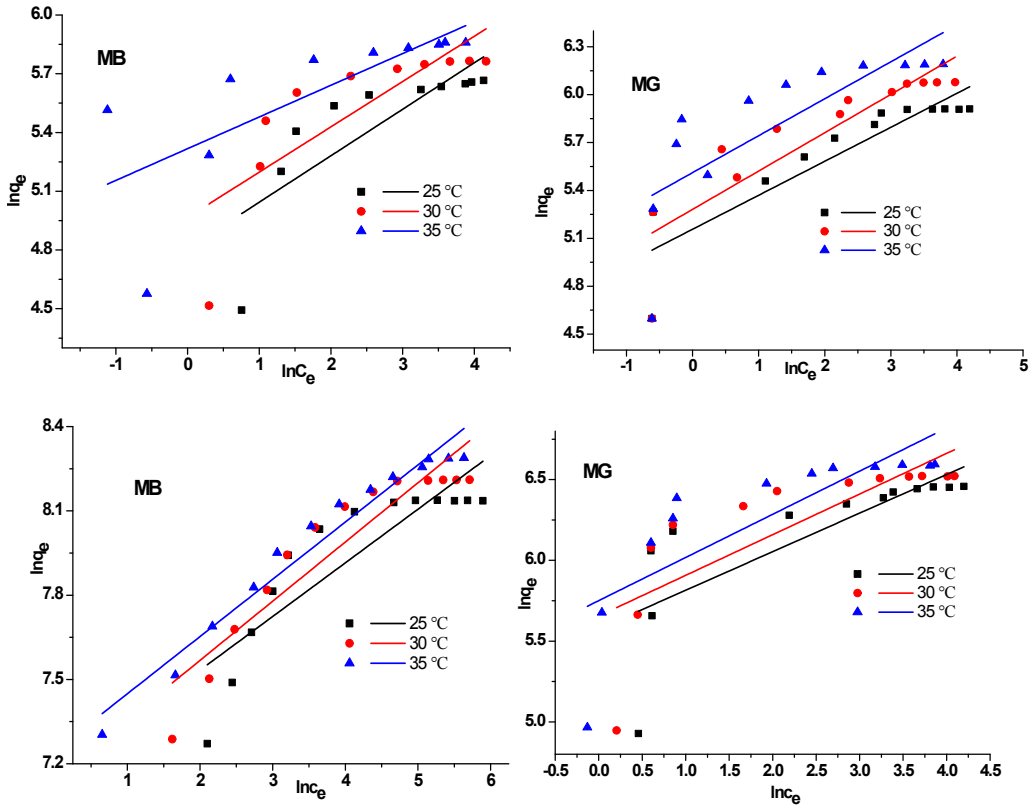


Figure S14 Linear regression of dyes adsorption by fitting the equilibrium adsorption data with the Freundlich adsorption mode (upper figures: Si-POP-1; lower figures: Si-POP-2).

Table S1 Freundlich isotherm parameters for adsorption of MB and MG on Si-POP-1 and Si-POP-2 at 25, 30 and 35 ^{o} C.

Adsorbents	Dyes	n	k_f	R^2
Si-POP-1	MG	4.697	173.6	0.79409
		4.166	196.7	0.76503
		4.321	247.6	0.574
	MB	4.216	122.4	0.59417
		4.324	143.5	0.60168
		6.176	203.8	0.48237
Si-POP-2	MG	4.190	264.1	0.55842
		3.975	285.9	0.56984
		3.743	314.4	0.59556
	MB	5.237	1276	0.74118
		4.746	1270	0.85697
		4.909	1402	0.95789

Table S2 Thermodynamic parameters for the MB and MG adsorption by Si-POP-1 and Si-POP-2.

Adsorbents	Dyes	T(K)	$\ln K_0$	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol.K)
Si-POP-1	MG	298.15	2.191	-5.433	64.55	234.4
		303.15	2.561	-6.454		
		308.15	2.967	-7.602		
Si-POP-1	MB	298.15	1.723	-4.271	48.08	175.42
		303.15	2.022	-5.095		
		308.15	2.301	-5.895		
Si-POP-2	MG	298.15	2.258	-5.597	38.43	147.5
		303.15	2.480	-6.250		
		308.15	2.720	-6.969		
Si-POP-2	MB	298.15	2.623	-6.503	42.74	164.9
		303.15	2.872	-7.238		
		308.15	3.137	-8.038		

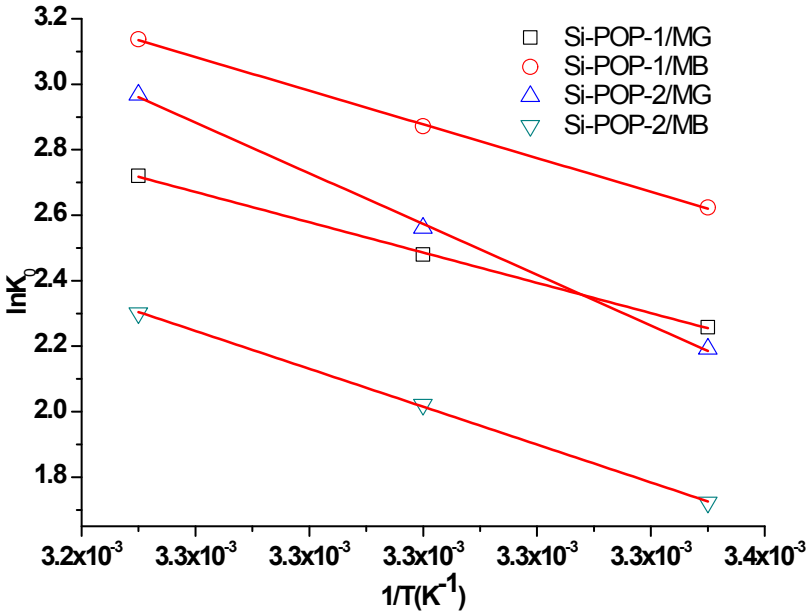


Figure S15 Plots of $\ln k_0$ versus 1/T for MB and MG adsorption onto Si-POP-1 and Si-POP-2.

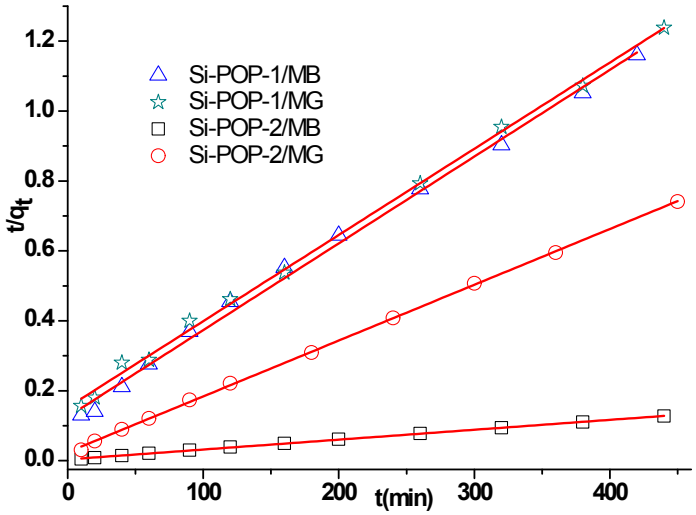


Figure S16 Plots of pseudo-second-order kinetics for adsorption of MB and MG on Si-POP-1 and Si-POP-2

Table **S3** Kinetic parameters fitted by pseudo-second-order kinetics equation for adsorption of MB and MG on Si-POP-1 and Si-POP-2 at 25 °C.

Adsorbents	Dyes	pseudo-first-order kinetics			pseudo-second-order kinetics		
		$k_1(min^{-1})$	$q_e(mg/g)$	R^2	$k_2(g/mg/min)$	$q_e(mg/g)$	R^2
Si-POP-1	MG	0.003700	11.58	0.9805	0.00003998	404.8	0.9975
	MB	0.01347	404.3	0.8805	0.00004901	403.2	0.9949
Si-POP-2	MG	0.01175	274.9	0.9523	0.0001049	625.0	0.9996
	MB	0.01040	1285	0.9686	0.00002192	3535	0.9995

Table S4 Adsorption selectivity of MB and MG on Si-POP-1 and Si-POP-2 at 25℃, 30℃ and 35℃.

Adsorbents	Dyes	T(K)	q_{max}(mg/g)	q_{exp}(mg/g)
Si-POP-1	MB	298.15	300.3	288.9
		303.15	330.0	318.5
		308.15	355.9	350.7
	MG	298.15	378.8	369.0
		303.15	450.4	436.1
		308.15	500.0	488.2
Si-POP-2	MB	298.15	3516	3415
		303.15	3806	3680
		308.15	4098	3980
	MG	298.15	662.2	637.6
		303.15	704.2	679.8
		308.15	757.6	730.9

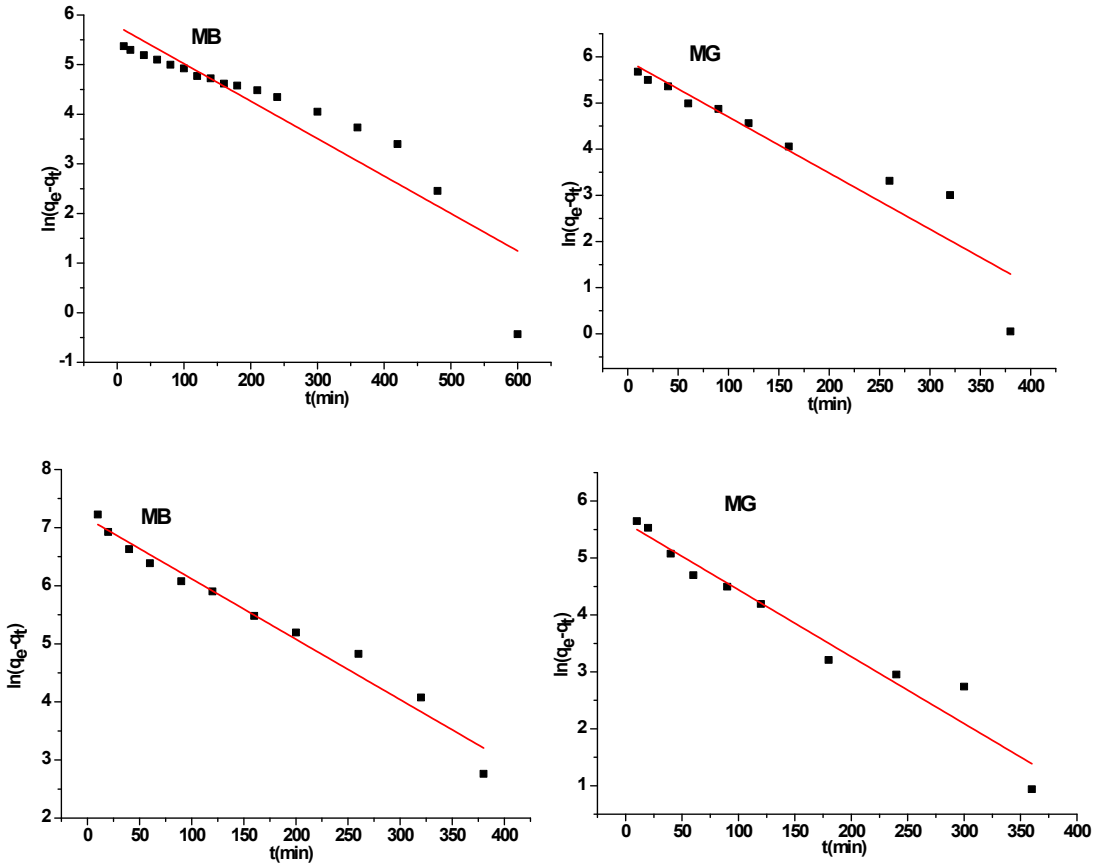


Figure S17 Plots of pseudo-first-order kinetic equation for the adsorption of MB and MG on Si-POP-1 and Si-POP-2 (upper figures: Si-POP-1; lower figures: Si-POP-2).

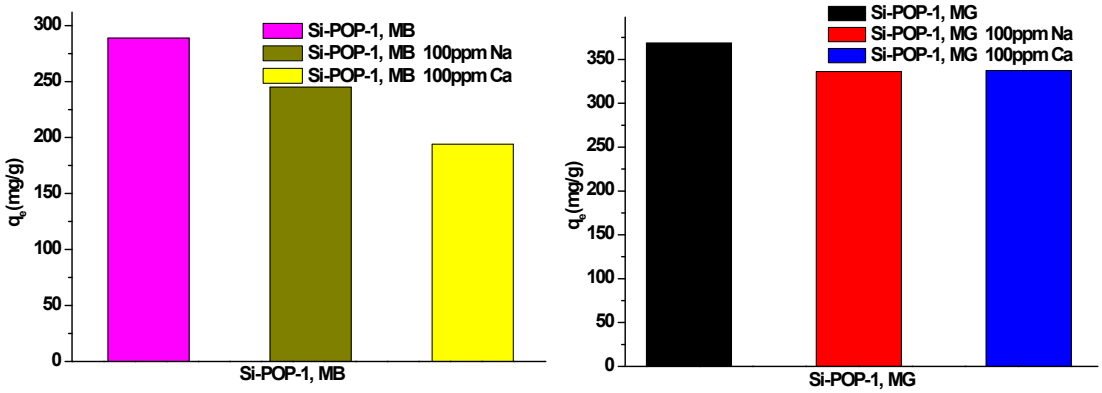


Figure S18 Effect of NaCl and $CaCl_2$ on the adsorption of MB and MG on Si-POP-1 at 25 °C.

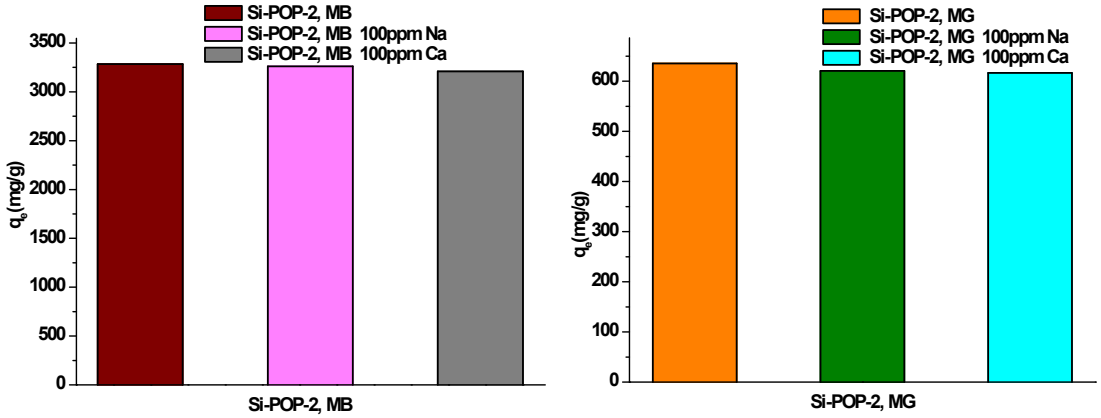


Figure S19 Effect of NaCl and $CaCl_2$ on the adsorption of MB and MG on Si-POP-2, at 25 °C.

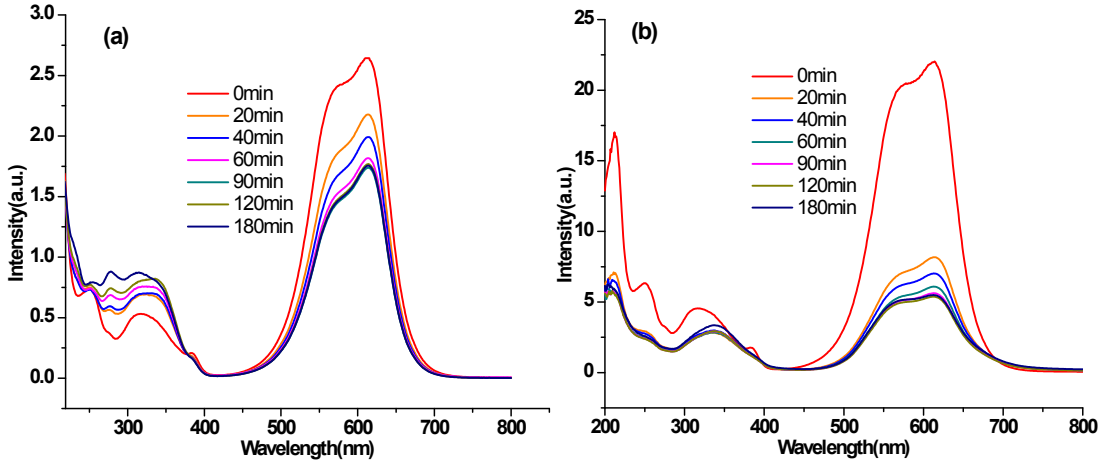


Figure S20 UV-vis spectra of BB7 aqueous solutions adsorbed by Si-POP-1 (a) and Si-POP-2 (b). Initial volume and concentration for (a): 50 mL, 25 mg/L BB7; (b): 50mL, 200 mg/L BB7. The mass of each adsorbent, Si-POP-1 or Si-POP-2, was 10 mg. Temperature was 25 °C.

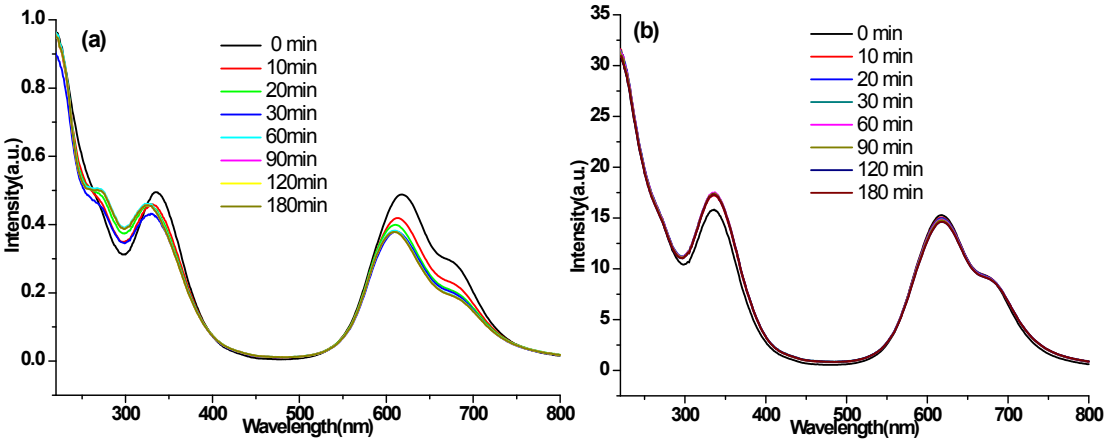


Figure S21 UV-vis spectra of AB8GX aqueous solutions adsorbed by Si-POP-1 (a) and Si-POP-2 (b), at 25 °C. Initial volume and concentration: (a) 75 mL, 25 mg/L AB8GX; (b): 75 mL, 250 mg/L AB8GX. The mass of each adsorbent, Si-POP-1 or Si-POP-2, was 10 mg.

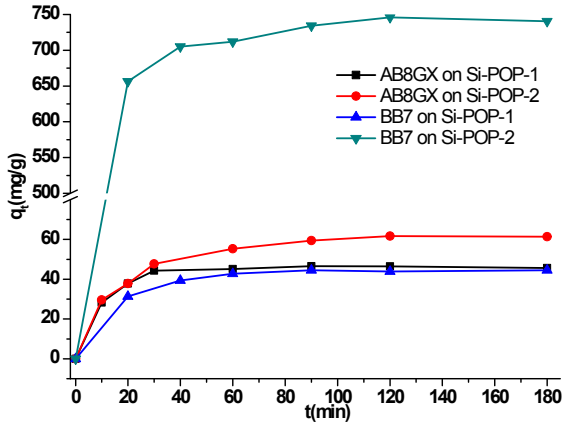


Figure S22 Plots of q_t *vs.* t for BB7 and AB8GX as adsorbed by Si-POP-1 and Si-POP-2 at 25 °C.

Reference

[1] A. Doddi, J. V. Kingston, V. Ramkumar, M. Suzuki, M. Hojo, M. N. Sudheendra Rao. *Phosphorus, Sulfur, and Silicon*, 2012, **187**, 343-356.