# Versatile supramolecular pH-tolerant hydrogels which demonstrate pH-dependent selective adsorption of dyes from aqueous solution

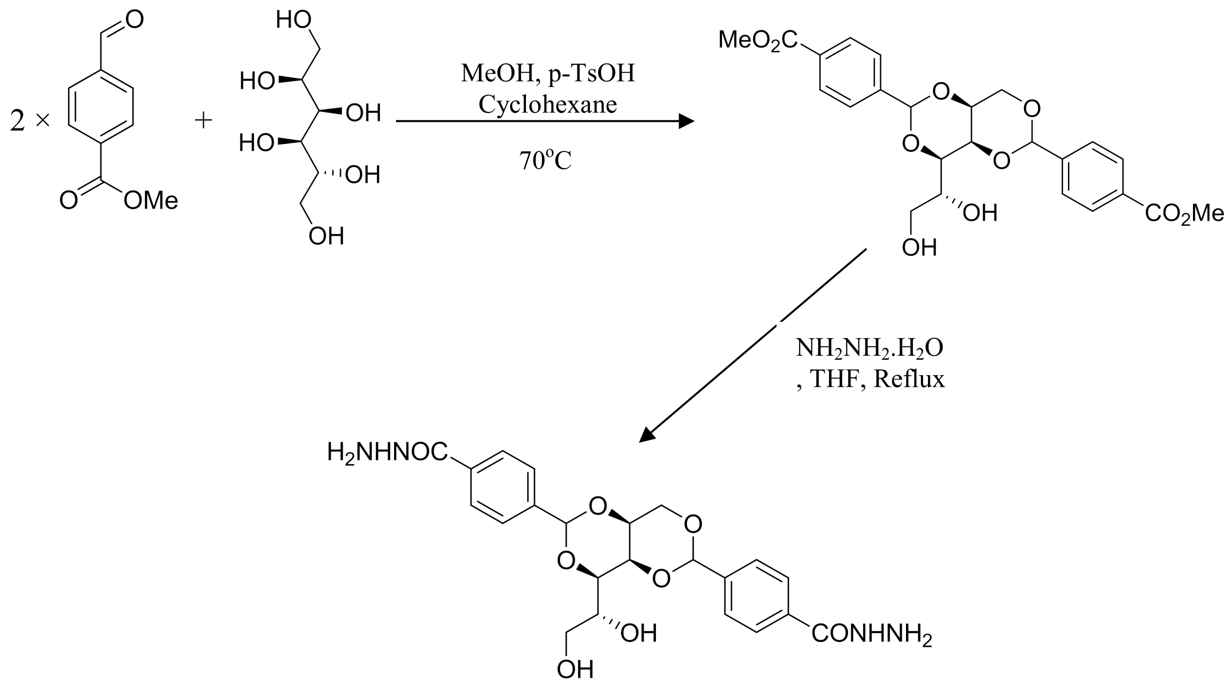
Babatunde O. Okesola and David K Smith*

Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK

## SUPPLEMENTARY INFORMATION

## Contents

## 1. Synthesis and Characterisation of DBS-$CO_2$H



**Scheme S1.** Synthesis of DBS-$CO_2$H

**General Experimental Methods.** DBS-$CONHNH_2$ was synthesised according to a two-step reaction procedure (see Scheme 1). All compounds required in the synthesis were purchased from standard commercial suppliers. $^1$H and $^{13}$C NMR spectra were recorded on a Jeol 400 spectrometer ($^1$H 400 MHz, $^{13}$C 100 MHz). Samples were recorded as solutions in deuterated NMR solvents as stated and chemical shifts (δ) are quoted in parts per million. Coupling constant values (*J*) are given in Hz. The level of assignment of $^1$H NMR spectra was achieved using model compounds, literature data and standard knowledge of $^1$H NMR. DEPT experiments were used to assist in the assignment of $^{13}$C NMR spectra. Positive and negative ion electrospray mass spectra were recorded on a Bruker Daltonics MicroTOF mass spectrometer. IR spectra were recorded on a PerkinElmer Spectrum Two FT-IR spectrometer. Melting points were measured on a Stuart SMP3 melting point apparatus and are uncorrected. Circular dichroism spectra were recorded on a Jasco J810 CD spectrophotometer. $T_{gel}$ values were recorded using a high precision thermoregulated oil bath. SEM was carried out on a LEO 1530 Gemini FEGSEM fitted with an Oxford Instruments 80mm X-Max SDD detector. UV-Vis Spectroscopy was performed on a Shimadzu UV-2401 spectrometer.

**Synthesis and Characterisation of DBS-$CO_2$Me.** D-Sorbitol (4.90 g, 0.0269 mol) was weighed into a 3-necked round-bottom flask fitted with Dean-Stark apparatus. Cyclohexane (35 ml) and methanol (10 ml) were added, and the mixture was stirred under $N_2$ at 50ºC for 20 min. 4-Methylcarboxylbenzaldehyde (7.50 g, 0.0457 mol) and *p*-toluene sulfonic acid hydrate (1.00 g, 5.26 mmol) were dissolved in methanol (20 ml) and stirred for 20 min at room temperature, before being added dropwise to the D-sorbitol mixture. The reaction temperature was increased to 70°C, and was stirred for 2 h, until most of the solvent was removed. The white paste formed was washed with methanol (3 x 100 ml). The crude product was dried under high vacuum for 2 h, then air-dried overnight. Mono- and trisubstituted derivatives were removed by washing with boiling water (4 x 100 ml) and boiling toluene (3 x 100 ml) respectively. Yield: 77% (8.37 g, 0.018 mmol). M.p: 210-213°C. $^1$H NMR (400 MHz, DMSO-*d*$_6$): δ 8.00-7.97 (m, 4H, Ar*H*), 7.63-7.58 (m, 4H, Ar*H*), 5.76 (s, 2H, Ar-C*H*), 4.96 (d, 1H, CHO*H*, *J* = 5.6), 4.50 (br, 1H, $CH_2$O*H*), 4.26-4.17 (q, 3H, sugar (overlap)), 4.01 (s, 1H, sugar), 3.89 (d, 1H, sugar, *J* = 9.2), 3.85 (s, 6H, OC$H_3$), 3.79 (br, 1H, sugar), 3.63-3.60 (m, 1H, sugar), 3.48-3.45 (m, 1H, sugar). $^{13}$C NMR (400 MHz, DMSO-*d*$_6$): δ 166.00 (*C*OO), 143.33 (aromatic *p*-*C*), 143.06 (aromatic *p*-*C*), 129.77-126.50 (aromatic *o*-*C*×2, aromatic *m*-*C*×2), 98.54-98.46 (Ph-*C*), 77.58 (*C*H), 70.18 (*C*H), 69.31 (*C*$H_2$), 68.53 (*C*H), 67.59 (*C*H), 62.56 (*C*$H_2$), 52.21 (*C*$H_3$). $\nu_{max}$ (cm$^{-1}$) (solid): 2956*w*, 1723*s*, 1435*w*, 1399*m*, 1276*s*, 1167*w*, 1093*s*, 1018*s*, 856*m*, 835*m*, 750*s*, 707*m*. ESI-MS (*m/z*) calc. for $C_{24}H_{26}O_{10}$ 474.152; found 475.160 (100% $[M+H]^+$), 497.143 (35% $[M+Na]^+$).

**Synthesis and Characterisation of DBS-CONHN$H_2$.** DBS-$CO_2$Me (1.1 g, 2.32 mmol) was dissolved in tetrahydrofuran (40 ml) and hydrazine monohydrate (6.19 g, 0.12 mol) was added to the reaction mixture. The reaction was allowed to proceed under reflux at 65°C for 10 h. TLC was used to monitor the completion of the reaction. After the reaction, the white precipitate formed was filtered off and washed thoroughly with deionised water (3 x 100 ml). The product was dried under high vacuum, then dried to a constant weight in a vacuum oven at 80ºC and pulverized. Yield 91% (1.0 g, 2.11 mmol). $^1$H NMR (400 MHz, DMSO-*d*$_6$): δ 9.77 (s, 2H, CON*H*N$H_2$), 7.46 -7.80 (m, 8H, Ar-H), 5.68 (s, 2H, ArC*H*), 4.94-4.96 (d, *J* = 5.6 Hz, CHO*H*, 1H), 4.45 (s, 2H, CONHN*H*$_2$), 4.41-4.45 ( t, *J* = 12 Hz, 1H, $CH_2$O*H*, 1H), 4.17 (q, *J* = 9.1 Hz, 1H, sugar), 4.14 (s, 1H, sugar), 3.95 (s, 1H, sugar), 3.85 (d, 1H, *J* = 9.2 Hz, sugar), 3.73-3.75 (m, 1H, sugar), 3.56-3.61 (m, 1H, sugar), 3.42-3.47 (m, 1H, sugar). $^{13}$C NMR (100 MHz, DMSO-*d*$_6$): δ 166.12 (C=O), 141.50, 134.06, 127.28 (all Ar), 99.20 (Ar-*C*H), 78.09, 70.63, 69.00 (all *C*H), 69.84, 63.10 (all *C*$H_2$). $\nu_{max}$ (cm$^{-1}$) (solid): 3294 (NH and

OH), 2870 (CH), 1633 (C=O), 1568 (C=C, aromatic), 1091 (C-O, acetal). ESI MS $C_{22}H_{27}N_4O_8$, *m/z* calculated 474.1751, found 475.1805 (100% $[M+H]^+$) .

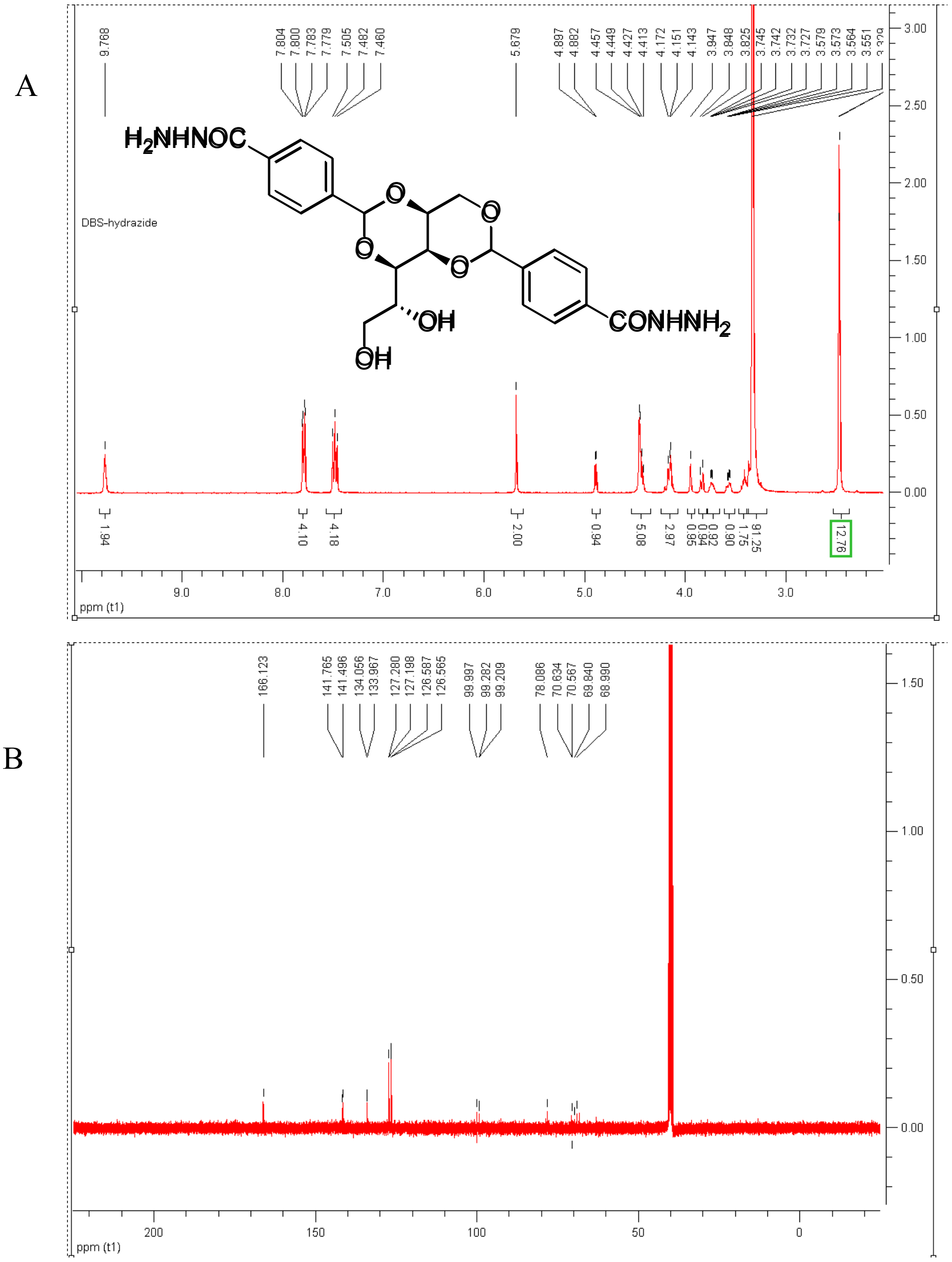


**Figure S1.** (A) $^1$H NMR and (B) $^{13}$C NMR spectral for DBS-$CONHNH_2$ in DMSO-$d_6$

## 2 $T_{gel}$ data

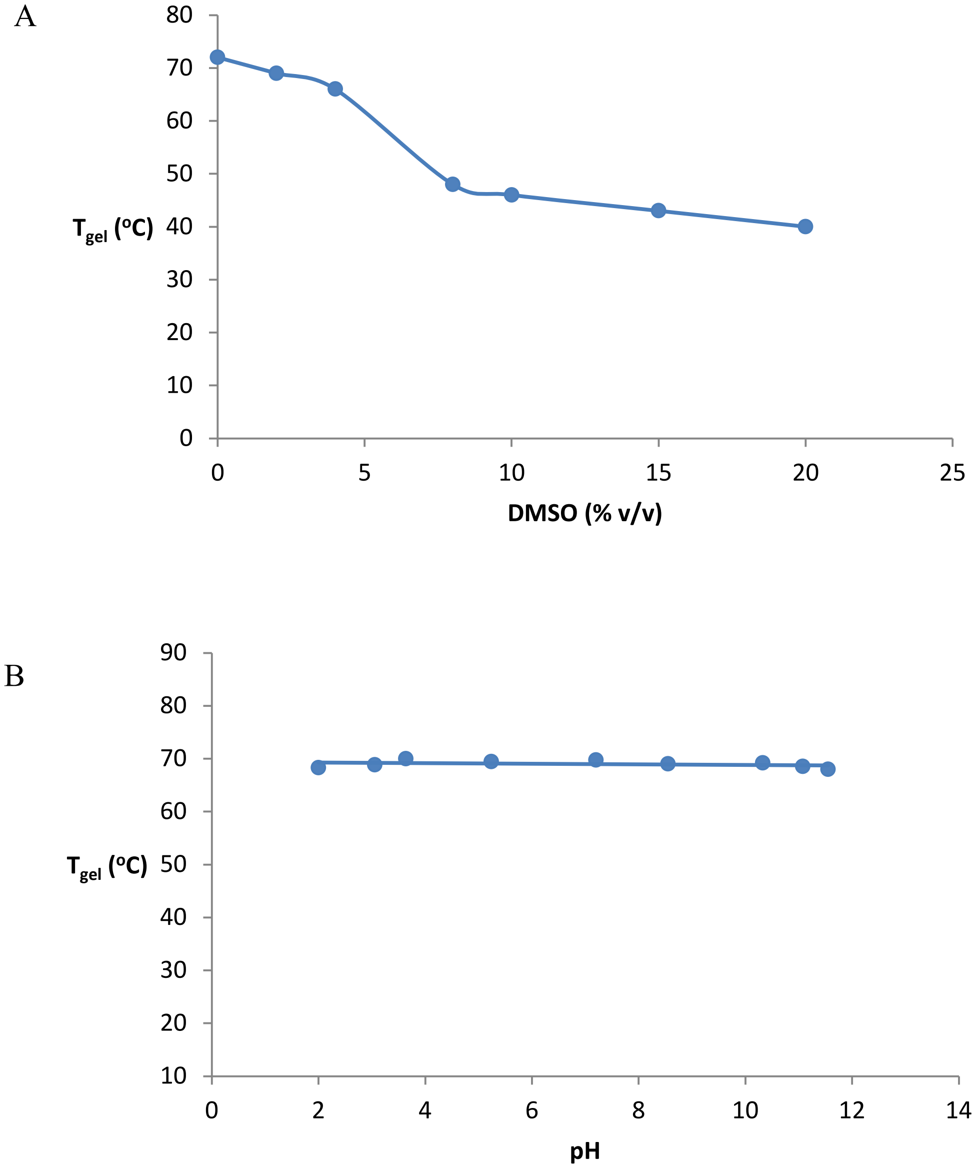


**Figure S2.** The $T_{gel}$ values of DBS-CONHNH$_2$ hydrogel (10 mM) as measured via tube inversion. (A) Effect of increasing concentration of DMSO as a co-solvent, and (B) Effect of pH.

## 3 VT CD Data

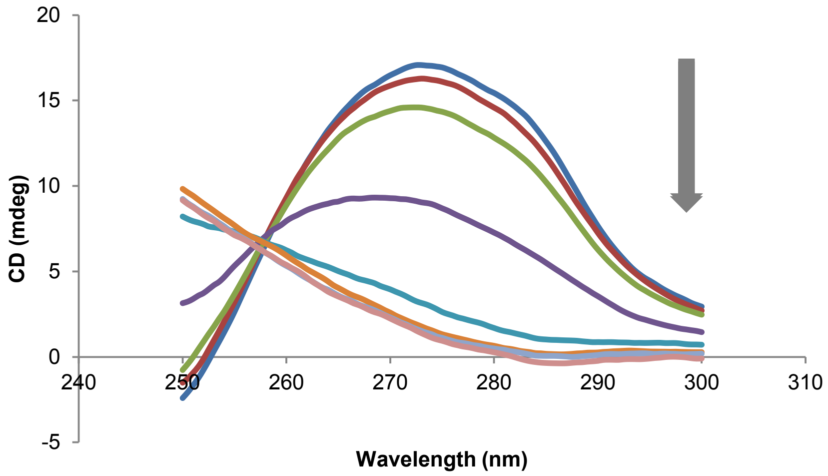
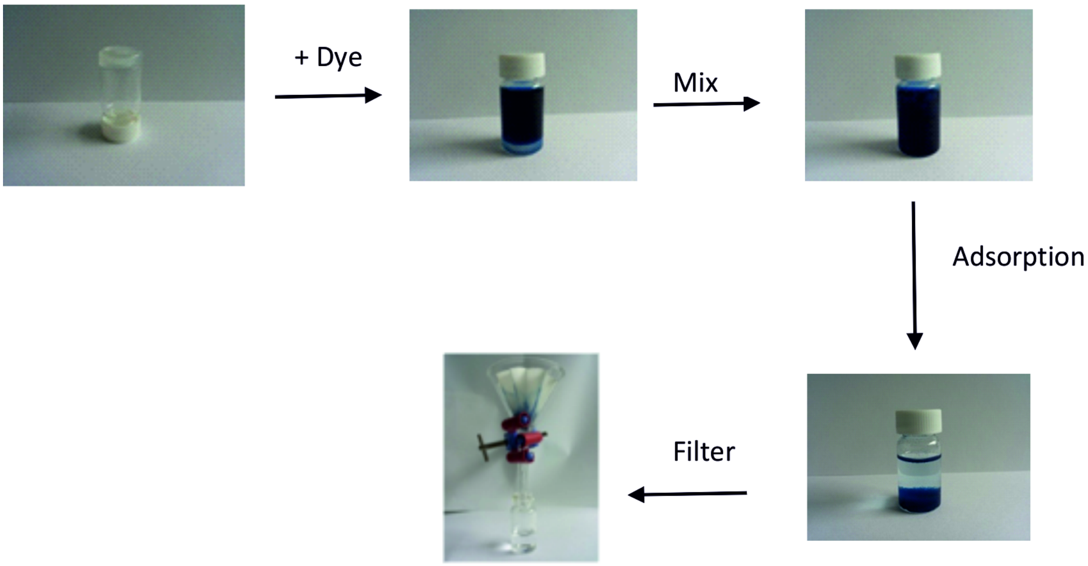


**Figure S3.** Variable temperature CD spectra of DBS-CONHNH$_2$. Arrow indicates increasing temerature from 20 to 90ºC in increments of 10ºC

## 4 Batch adsorption design



**Scheme S2.** Batch process for the adsorption of dyes (Methylene blue, Acid blue 25 and Naphthol blue back) onto DBS-CONHNH$_2$ hydrogel.

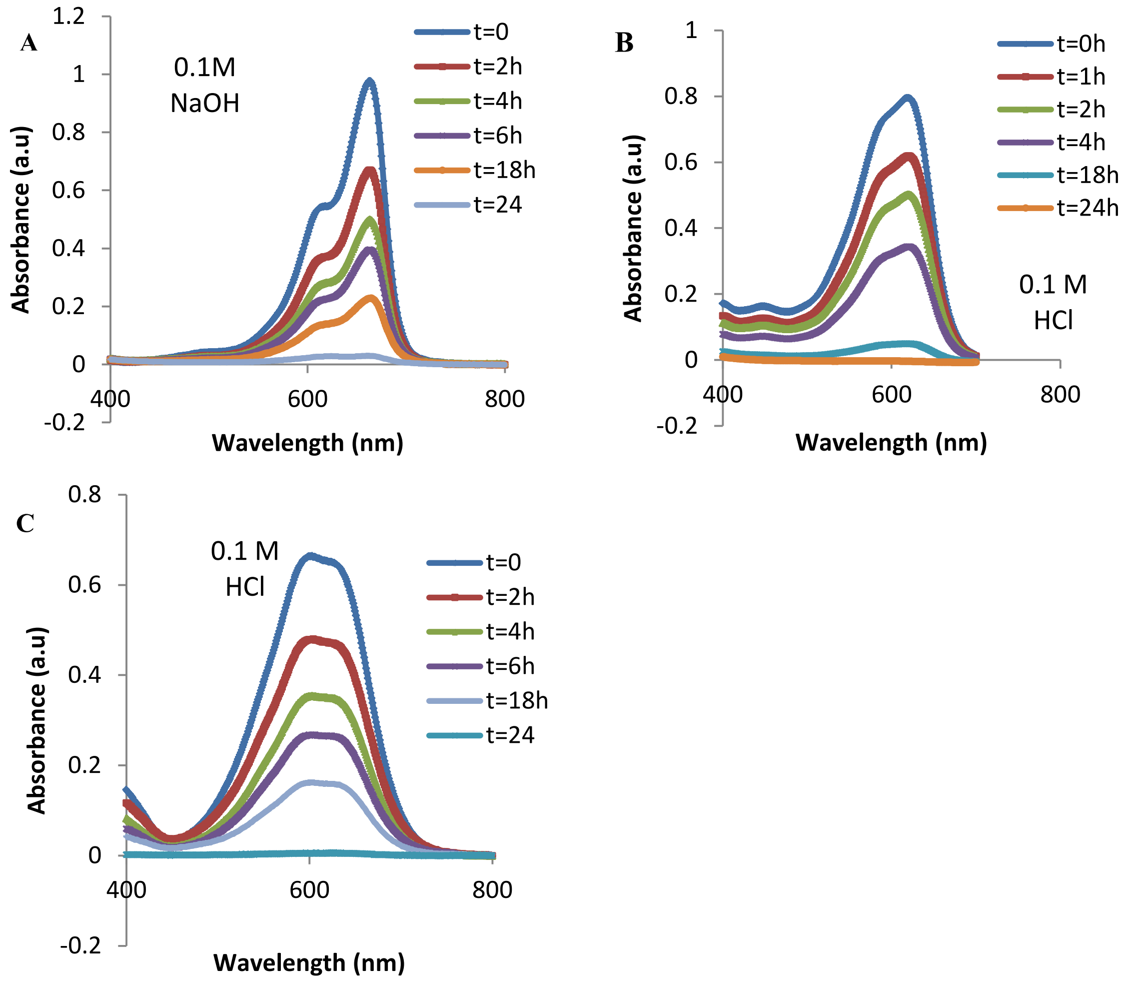


**Figure S4.** Typical UV-Vis spectra for initial time-dependent adsorption studies of (A) Methylene Blue (B) Naphthol Blue Black (C) Acid Blue 25 onto DBS-CONHNH$_2$ hydrogel. These spectra are exemplars, and were measured under different conditions to the kinetic experiments described in Section 4.

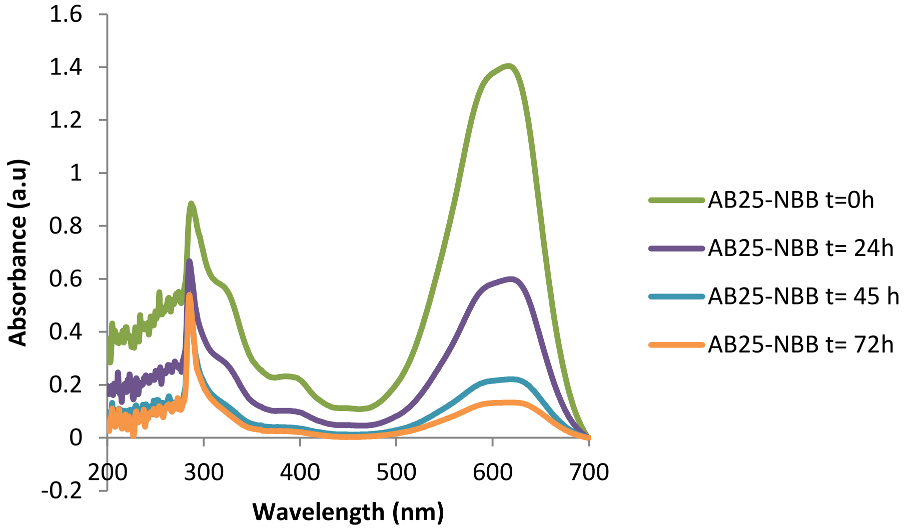


**Figure S5.** Typical UV-Vis spectra for initial time-dependent adsorption studies of a mixture of Naphthol Blue Black and Acid Blue 25 onto DBS-CONHNH$_2$ hydrogel, showing the simultaneous adsorption of both dyes.

## 5 Batch Adsorptive Kinetics of Dyes onto DBS-CONHNH$_2$ hydrogel.

The amount of dye adsorbed was monitored by adding 5 mL of each of the dye solutions; Methylene Blue (MB, 1.2 g/l), Acid Blue 25 (AB25 1.54 g/l) and Naphthol Blue Black (NBB, 1.2 g/l) to a vial containing the hydrogel adsorbent (0.8 % wt/v, 8 mg in 1 ml). The time-dependent study of the adsorption of dyes was carried out under various pH conditions at room temperature. The pH of the dye solutions were adjusted with HCl (0.1 M, aq) and NaOH (0.1 M, aq). A sample of the supernatant (10 µl) was taken, diluted and the concentration of dye remaining in the solution was hence determined at various time intervals using UV-Vis spectroscopy. The data obtained were used to compute the adsorption kinetics. The maximum dye uptake by the hydrogels in this experiment was determined at the point where there was no more significant adsorption and this was chosen to be close to the maximum saturation values found previously for maximum gel adsorption.

The maximum dye uptake was determined using equation (1).[1]

$$q_e = (Co - Ce)V/m \qquad (1)$$

$q_e$ is the amount of dye adsorbed (mg/g), m is the weight of adsorbent used (g), $C_e$ is the equilibrium concentration of dye in solution (mg/L), $C_o$ is the initial dye concentration (mg/L) in solution, and V is the volume (L) of aqueous dye solution treated.

According to Ho and Mckay,[2] pseudo second-order kinetics is described by eq. (2-3);

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (2)$$

where $q_e$ and $q_t$ are the amounts (mg/g) of dye adsorbed per unit mass of gelator at equilibrium and at time t respectively, and $k_2$ is the pseudo second-order adsorption constant (g/mgh).

Upon application of boundary condition t= 0 to t=t and $q_t$=0 to $q_t$=$q_t$ , followed by integration this results in:

$$\frac{t}{q_t} = \frac{1}{K_2 {q_e}^2} + t/q_e \qquad (3)$$

Manipulating the data with this equation indicates that if pseudo second order kinetics hold, then the plot of $\frac{t}{q_t}$ vs t should give a straight line, with a gradient of $1/q_e$ and and intercept of $1/k_2{q_e}^2$.

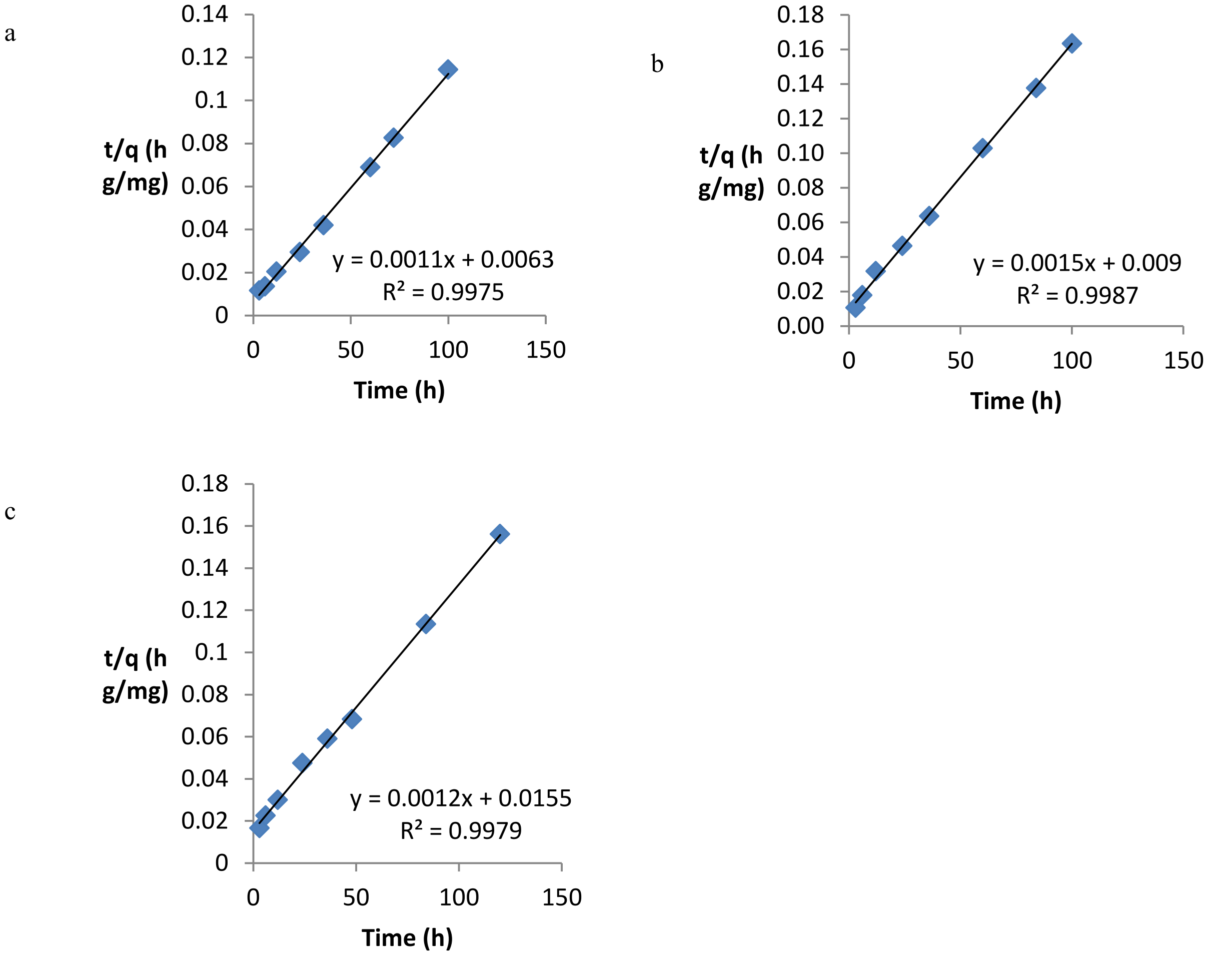


**Figure S6.** Pseudo second-order adsorption kinetics of (a) Acid blue 25 (AB25) (b) Naphthol blue black (NBB) (c) Methylene blue (MB).

## 6 References

1. K. G. Bhattacharyya and A. Sharma, *J. Environ. Manage.*, 2004, **71**, 217-229.
2. Y. S. Ho and G. McKay, *Can. J. Chem. Eng.*, 1998, **76**, 822-827.