Electronic Supplementary Materials (ESI) for Chemical Communications

# Hydrophilic Polymer Nanofibre Networks for Rapid Removal of Aromatic Compounds from Water

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## 1. Materials

### 1-1. Polymers

Polystyrene ($M_w$ 208,000) was obtained from *Wako Pure Chemical*. Polysulfone ($M_w$ 60,000), polycarbonate ($M_w$ 36,000), polyethersulfone (Melt flow index: 3.98 g/10 min at 320°C), and poly(*p*-phenylene oxide) ($M_w$ 50,000) were obtained from *Scientific Polymer Products*. Polyetherimide ($M_w$ 30,000) was obtained from *Polysciences*.



Polystyrene (PS)          Polysulfone (PSF)          Polycarbonate (PC)



Polyethersulfone (PES)          Poly(*p*-phenylene oxide) (PPO)



Polyetherimide (PEI)
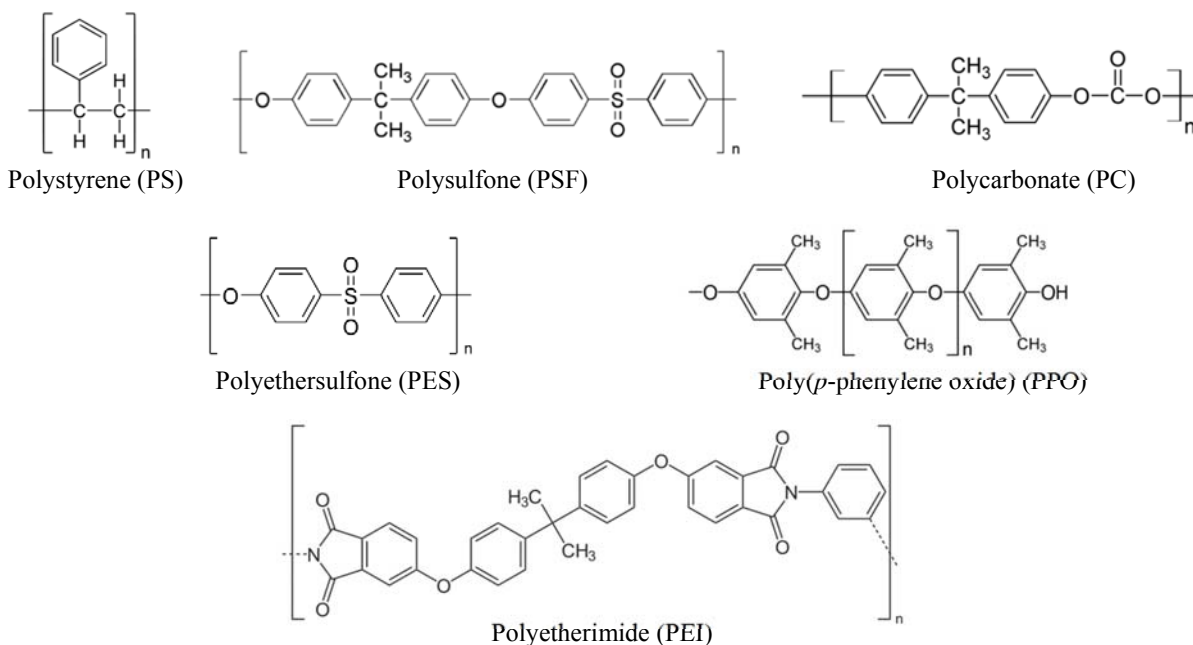
### 1-2. Solvents

N,N-dimethylformamide (DMF, $M_w$ 73.09, GC purity 99.5%), *o*-dichlorobenzene (DCB, $M_w$ 147.0, GC purity 99%), chloroform ($M_w$ 119.38, GC purity 99%), cyclohexanone ($M_w$ 98.14, GC purity 99%), nitrobenzene ($M_w$ 123.11, GC purity 99.5%), N-methyl-2-pyrrolidone (NMP, $M_w$ 99.13, GC purity 99%), and methanol ($M_w$ 32.04, GC purity 99.8%) were obtained from *Kanto Chemical* and used without further purification.

## 2. Fabrication Procedures of Polymer Nanofibre Networks

Ultrafine nanofibrous polymer network structures were prepared by means of a newly developed nanocrystallization technique in a frozen polymer solution (Samitsu *et al.*, *Nature Communications*, **2013**, *4*, 2653). When the temperature of the polymer solution is rapidly decreased from room temperature to that of liquid $N_2$, the solvent molecules are frozen among vitrified polymer chains. The glassy polymer solution is then slowly heated to a temperature slightly lower than the melting point of the solvent in order to induce nanocrystallization of the solvent molecules. By extracting the crystallized solvent molecules with a poor solvent (usually methanol), a mesoporous polymer nanofibre network is obtained in the poor solvent. In this work, such polymer nanofibre networks were prepared by the following procedures.

### 2-1. Polymer solutions

PS was dissolved in N,N-dimethylformamide (DMF). PSF was dissolved in *o*-dichlorobenzene (DCB). PC and PPO solutions were prepared with chloroform. PES was dissolved in cyclohexanone, and PEI was dissolved in a 1:1 w/w mixture of nitrobenzene and N-methyl-2-pyrrolidone (NMP). When the dissolution rate of the polymer was not high at room temperature, the solution temperature was gradually elevated to 70°C. The concentration of these polymer solutions was 20 wt%.

### 2-2. Rapid freezing of polymer solution

The prepared polymer solution (10 mL) was applied as a coating to the inner surface of a 100 mL cylindrical glass bottle by rotating the bottle horizontally to make a thin layer of the polymer solution. The glass bottle was then immediately immersed into liquid $N_2$ and allowed to stand for 15 min to make the deep-frozen polymer solution.

### 2-3. Solvent exchange and drying

90 mL of methanol pre-cooled at −80°C was added to the above frozen polymer solution, and subsequently transferred to the refrigerator pre-cooled at −80°C and kept for five days to substitute the good solvent with methanol. Then the solidified polymer was brought to room temperature and the methanol was decanted off. The polymer was washed with methanol several times for two days at room temperature. Finally, the methanol was decanted completely and dried in a vacuum chamber for 12 h.

## 3. Structural Characterization

### 3-1. SEM observation

Scanning electron microscopy (SEM) images of the polymer nanofibre networks were obtained using a Hitachi S-4800. To prepare the specimens, the vacuum-dried sample was immersed into ethanol to remove air inside the mesopores. Then the sample was broken in liquid $N_2$ to analyze a cross-section. This freeze-fracturing was essential to prevent elongation of the nanofibrous structure. The specimen was attached to an SEM sample holder and a 2-nm-thick platinum layer was deposited using a Hitachi E-1030 ion sputter in order to prevent electric charging of the specimen. The deposition was conducted at room temperature under an argon atmosphere of 10 Pa or lower and at a current density of 10 mA. All images were obtained at accelerating voltages of 5 kV or 10 kV.

### 3-2. BET and BJH analyses

The specific surface areas of the mesoporous polymer nanofibre networks were analyzed based on $N_2$ gas adsorption isotherms. The measurements were conducted using a BEL Japan Belsorp-max. The mesoporous polymers were thoroughly degassed under vacuum and injected into the sample port. The specific surface area was determined by means of the Brunauer-Emmett-Teller (BET) model from the low-pressure regions ($p/p_0 < 0.3$) of the $N_2$ adsorption isotherms.

## 4. Surface Modification

### 4-1. Sulfonation

Mesoporous PS (1 g) was added to 10 mL of ethanol and weakly stirred for 10–15 min to remove air inside the mesopores. The ethanol was quickly decanted, and then 5 mL of conc. $H_2SO_4$ (*Kanto Chemical*, 96% grade) was added to the glass bottle. The sulfonation was carried out over different periods (2–12 h) with constant stirring at a certain temperature (30–50°C). The sample was then removed from the bottle and washed with methanol several times, followed by washing with deionized water until the pH of the rinsing water became around neutral. As the ratio of sulfonation increased, the mesoporous structure became prone to damage during the drying process. The deterioration of the mesopores was partially preventable by immersing the sample into methanol before vacuum drying.

Without the use of a catalyst such as $Ag^+$, the sulfonation reaction proceeded very slowly. This made it possible to uniformly modify the inner surfaces of mesoporous PS. In addition, strong osmotic pressure between *in situ* ethanol and conc. $H_2SO_4$ accelerated the diffusion of $H_2SO_4$ into the mesopores. Sulfonation of mesoporous PC was readily achieved using sulfuric acid acetyl ester produced from acetic anhydride (3 mL) and conc. $H_2SO_4$ (1 mL) in methanol (16 mL). However, sulfonation of PSF was not achieved with either conc. $H_2SO_4$ or sulfuric acid acetyl ester. Therefore, it was carried out using 0.3 mL of chlorosulfuric acid (*Wako*, 97% grade) in *n*-hexane (7 mL). Caution: this chemical reacts violently with water to yield sulfuric acid and HCl. Mesoporous PPO was sulfonated with sulfuric acid acetyl ester, whereas mesoporous PES was sulfonated with chlorosulfonic acid using similar methods to those used for PC and PSF, respectively (Smitha *et al.*, *J. Memb. Sci.*, **2003**, *225*, 63-76). Through these sulfonation procedures, mesoporous polymers were made sufficiently hydrophilic to quickly absorb water.

### 4-2. Determination of ion exchange capacity

The ion exchange capacity (*IEC*) of sulfonated mesoporous polymers was defined as the number of replaceable $H^+$ ions in a certain weight of the polymer in aqueous medium. For the titration experiments, 100 mg of sulfonated mesoporous PS was dispersed in 10 mL of 1 M aqueous NaCl solution and the solution was stirred for 24 h at 30°C. The mesoporous polymer was then removed from the solution. The resulting NaCl solution containing HCl was titrated with 0.1 M aqueous NaOH using a pH meter. The *IEC* value was calculated from the following equation:

$$IEC \text{ (meq/g)} = \frac{[Volume\ of\ NaOH\ \text{(mL)} \times Concentration\ of\ NaOH\ \text{(M)}]}{Weight\ of\ dried\ polymer\ \text{(g)}}$$

where the units are mmol/g or meq/g. The degree of substitution ($DS$) was defined as the average number of substituted sulfonic acid groups per monomer unit. In case of PS, the value was calculated from the following equation (Othman $et\ al.$, $Malaysian\ Polymer\ Journal$, $\mathbf{2007}$, $2$, 10-28):

$$DS = \frac{104 \times IEC}{1000 - (184 \times IEC) + (104 \times IEC)}$$

In this equation, the figures 104 and 184 represent the molecular weight of the monomer unit and that of the sulfonated monomer unit. The molar number of the introduced sulfonate groups per gram ($N_s$) and the molar equivalent weight polymer per sulfonate group ($E_w$) were calculated as follows:

$$N_s = IEC \text{ (mmol/g)} \bullet N_A \text{ (mol}^{-1})$$

$$E_w \text{ (g/mmol)} = 1/IEC \text{ (mmol/g)}$$

where $N_A$ is Avogadro's constant. Table S1 summarizes the $IEC$, $DS$, $N_S$, and $E_w$ values for PS nanofibre networks sulfonated at different times and temperatures.

**Table S1.** Sulfonation of PS nanofibre networks at different temperatures and for different times.

| Temp. | Time (h) | $IEC$ (meq/g) | $DS$ | $N_S$ ($\times 10^{18}$) | $E_w$ (g/mmol) |
|---|---|---|---|---|---|
| | 2 | 0.011 | $1.15 \times 10^{-3}$ | 6.63 | 90.9 |
| | 4 | 0.013 | $1.35 \times 10^{-3}$ | 7.83 | 76.9 |
| 30°C | 6 | 0.016 | $1.67 \times 10^{-3}$ | 9.64 | 62.5 |
| | 8 | 0.020 | $2.08 \times 10^{-3}$ | 12.0 | 50.0 |
| | 12 | 0.024 | $2.50 \times 10^{-3}$ | 14.5 | 41.7 |
| | 2 | 0.019 | $1.98 \times 10^{-3}$ | 11.4 | 52.6 |
| | 4 | 0.023 | $2.40 \times 10^{-3}$ | 13.9 | 43.5 |
| 40°C | 6 | 0.027 | $2.81 \times 10^{-3}$ | 16.3 | 37.0 |
| | 8 | 0.030 | $3.13 \times 10^{-3}$ | 18.1 | 33.3 |
| | 12 | 0.040 | $4.17 \times 10^{-3}$ | 24.1 | 25.0 |
| | 2 | 0.034 | $3.55 \times 10^{-3}$ | 20.5 | 29.4 |
| | 4 | 0.040 | $4.17 \times 10^{-3}$ | 24.1 | 25.0 |
| 50°C | 6 | 0.046 | $4.80 \times 10^{-3}$ | 27.7 | 21.7 |
| | 8 | 0.053 | $5.54 \times 10^{-3}$ | 31.9 | 18.9 |
| | 12 | 0.063 | $6.59 \times 10^{-3}$ | 37.9 | 15.8 |

Even at the smallest degree of sulfonation, wettability of polymer nanofibre network and adsorption kinetics were significantly improved. The adsorption kinetics was especially improved in the dilute aqueous solutions of aromatic compounds.

**5. Adsorption Equilibrium and Thermodynamic Tendencies**

**5-1. Equilibrium adsorption isotherms**

The equilibrium adsorption isotherms of sulfonated polystyrene nanofibre network for phenol, *m*-cresol, pyridine, and aniline in water are given in Fig. S1. The symbols $q_e$ and $C_e$ represent the equilibrium adsorption amount and equilibrium concentration. The adsorption isotherms were obtained by tracing the decrease in concentration of the corresponding aromatic compound with a UV-vis absorption spectrometer. A typical adsorption experiment was conducted by adding 50 g/L of the sulfonated polystyrene nanofibre network (adsorbent) to an aqueous solution of an aromatic compound (adsorbate) at various concentrations ranging from 10 mg/L to 1000 mg/L. After monitoring the adsorption of the compounds for 72 h, we confirmed that equilibrium adsorption was reached within 4 h. In all cases, the adsorbate was strongly captured at low temperature (30°C). This indicates that the interaction between the adsorbate and the polymer chains is considerably reduced at high temperature, as compared with the decrease in the affinity of water with the adsorbate at that temperature.
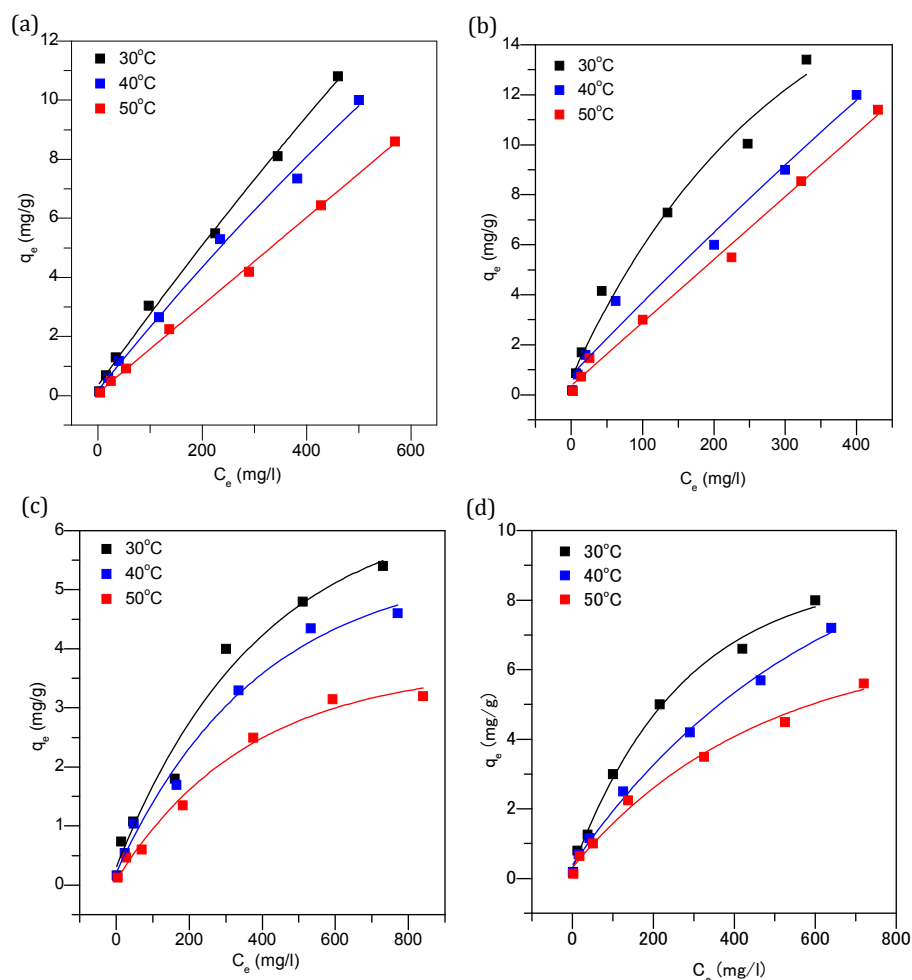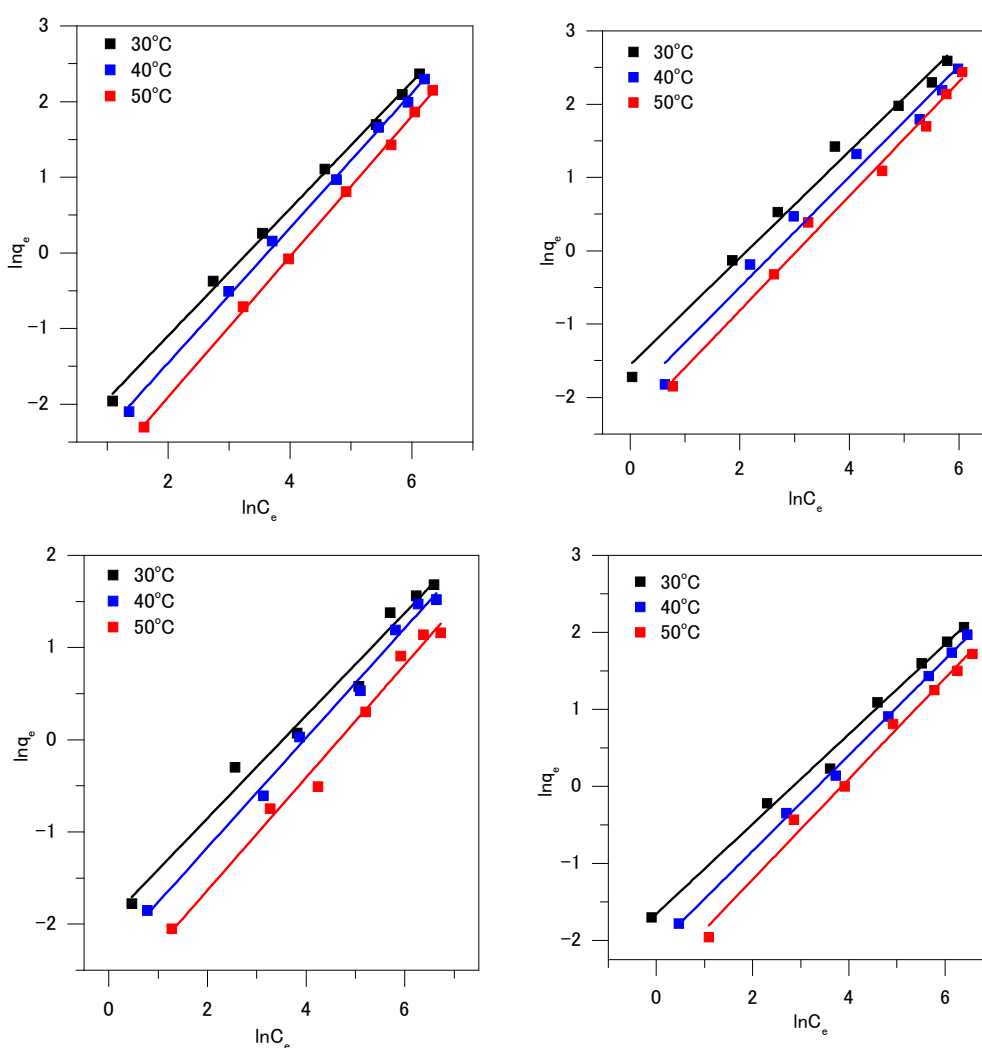


**Figure S1.** Equilibrium adsorption isotherms of sulfonated polystyrene nanofibre networks (0.011 meq/g). (a) Phenol, (b) *m*-cresol, (c) pyridine, and (d) aniline. The adsorption period is 4 h.

**5-2. Characterization using the Freundlich equation**

The equilibrium adsorption data were analyzed by fitting them to the linear Freundlich adsorption model (Freundlich, *Z. Phys. Chem.*, **1906**, *57*, 385). The results are shown in Fig. S2. The Freundlich equation is given by:

$$\ln q_e = \ln K_f + 1/n \ln C_e$$

where $K_f$ and $n$ indicate the adsorption capacity and adsorption intensity. These results are summarized in Table 1 of our article and discussed there.



**Figure S2**. Linear Freundlich adsorption isotherms of (a) phenol, (b) *m*-cresol, (c) pyridine, and (d) aniline obtained for sulfonated polystyrene nanofibre networks (0.011 meq/g) at different temperatures.

**5-3. Van't Hoff plots**

To derive the enthalpy changes ($\Delta H$) of the respective adsorptions, the $\ln C_e$ values were plotted against the inverse of temperature (in K) for a given equilibrium adsorption amount ($q_e$). This plot is known as the van't Hoff plot, which is given by the following equation (Li *et al.*, *J. Colloid Interface Sci.*, **2004**, *271*, 47-54).

$$\ln C_e = \left(\frac{\Delta H}{RT}\right) + \ln K_f$$

Figure S3 shows the van't Hoff plots of sulfonated polystyrene nanofibre networks (*IEC*: 0.011 meq/g) for the adsorption of phenol, *m*-cresol, pyridine, and aniline. $\Delta H$ values were calculated from the slope of the plot and are summarized in Table 1 of our article.
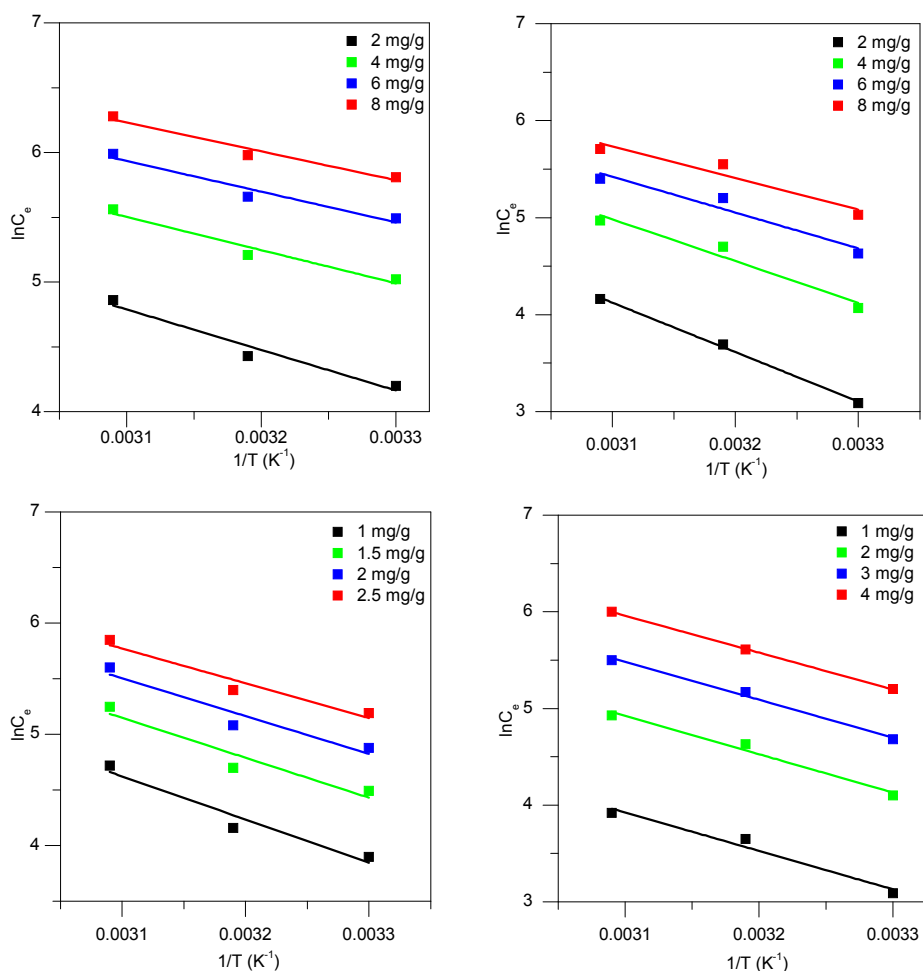


**Figure S3**. Van't Hoff plots of sulfonated polystyrene nanofibre networks for the adsorption of (a) phenol, (b) *m*-cresol, (c) pyridine, and (d) aniline.

The adsorption kinetics of phenol, *m*-cresol, pyridine, and aniline were analyzed based on the decrease in concentration of the corresponding aromatic compound with time using a UV-vis absorption spectrometer. A typical adsorption experiment involved the addition of 50 g/L of the sulfonated polystyrene nanofibre network (adsorbent) into an aqueous solution of an aromatic compound (adsorbate) at a concentration of 100 mg/L. The kinetic data were plotted with a linear pseudo-second-order kinetic model. This model is given by the following equation (Srivastava *et al.*, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, **2006**, 272, 89-104):

$$\frac{t}{q_t} = \frac{1}{k_2 q_{ke}^2} + \frac{1}{q_{ke}} t$$

where $q_t$ is the amount of the adsorbate adsorbed by the adsorbent at time $t$ and $q_{ke}$ is the equilibrium adsorption amount obtained by analyzing the adsorption kinetics data. The resultant plots are shown in Fig. S4. The second-order rate constants ($k_2$) were calculated from the slope of the plot ($1/q_{ke}$) against time. All of the rate constants are summarized in Table 2 of our article.
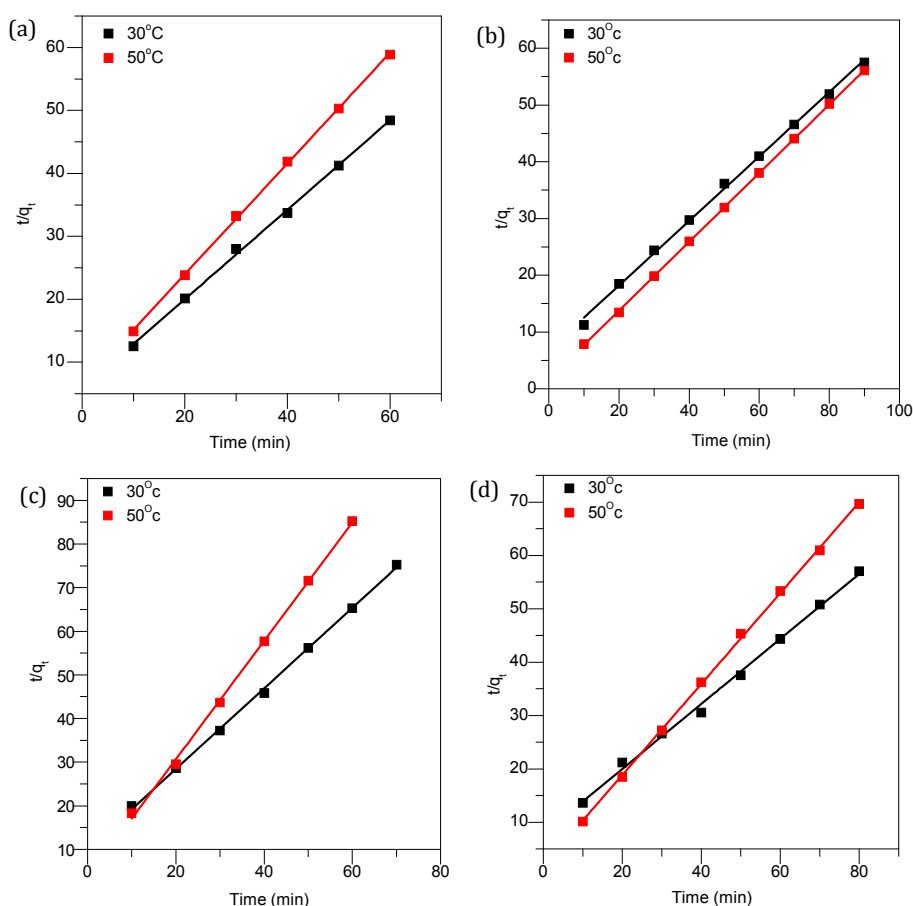


**Figure S4**. Linear pseudo-second-order kinetic plots for adsorption of (a) phenol, (b) *m*-cresol, (c) pyridine, and (d) aniline.