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Selective dye adsorption by chemically-modified and thermally-treated polymers of intrinsic microporosity

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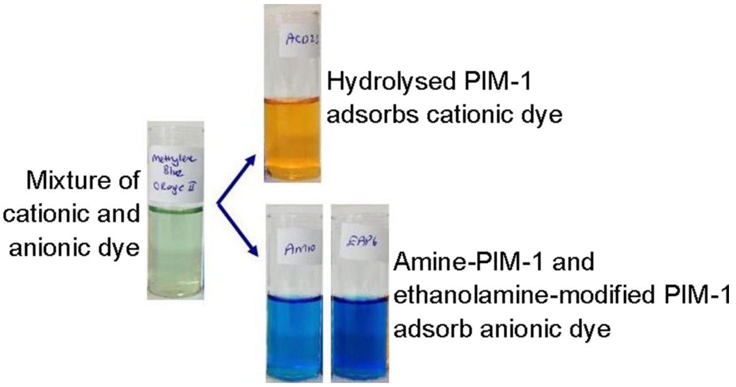
GRAPHICAL ABSTRACT



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ABSTRACT

Nitrile groups in the polymer of intrinsic microporosity PIM-1 were modified by base-catalysed hydrolysis, by reaction with ethanolamine and diethanolamine, and by reduction to amine, and the products investigated for their ability to take up a range of dyes from aqueous or ethanolic solution. Hydrolysed products exhibited selectivity for cationic over anionic species, while other products showed the reverse selectivity. At low pH, amine-PIM-1 adsorbed more than its own weight of the anionic dyes Orange II and Acid Red I from aqueous solution. It was demonstrated that adsorbed Orange II can be removed with basic ethanol. Mixtures of oppositely charged dyes undergo precipitation, but selective adsorption of one dye leads to dissolution of the other from the precipitate. Thermal treatment of the chemically modified polymers at 300 °C for 48 h in an inert atmosphere led to structural changes that reduced the dye adsorption capacity. On the basis of a combination of thermogravimetric and elemental analysis with ATR-IR and NMR spectroscopy, feasible structures are suggested for the thermally-treated polymers.

1. Introduction

The provision of clean water represents a major global challenge and there is a need for efficient ways to remove dyes and other organic pollutants from wastewater [1–3]. Furthermore, chemical and biotechnological manufacturing processes may require the selective recovery of specific organic compounds from mixtures in solution [4]. Solid-state absorbents with tailorable selectivity provide a straightforward method of isolating organic species. Adsorbent materials may potentially be utilised in an adsorption/desorption process, or as thin films in a membrane process allowing continuous operation and in-situ recovery.

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Polymers of intrinsic microporosity (PIMs) are glassy polymers with backbones composed of fused rings, interrupted by sites of contortion such as spiro-centres [5]. As there are no single bonds in the backbone about which rotation can occur, but the chains nevertheless have contorted structures, the macromolecules cannot pack efficiently in the solid state. Consequently, the polymers possess high free volume and behave like microporous materials as defined by IUPAC (pore size <2 nm) [6]. The archetypal PIM, referred to as PIM-1 (Fig. 1), is soluble in solvents such as chloroform and tetrahydrofuran, and can be processed into a variety of forms, including powders, fibres and membranes [7,8]. PIM-1 has been extensively investigated as a membrane material, and for membrane gas separation it helped to define Robeson's 2008 upper bound of performance for important gas pairs such as O_2/N_2, CO_2/CH_4 and CO_2/N_2 [9]. The first commercial application of PIM-1 is in an organic vapour sensor, used as an end-of-life indicator for vapour adsorbing cartridges [10,11].

PIM-1 is an organophilic polymer. In membrane form it can be applied in pervaporation of aqueous solutions of phenol, ethanol, butanol or other volatile organic compounds, to give a permeate vapour enriched in the organic component [8,12–15]. It may also be applied in organic solvent nanofiltration, allowing permeation of certain species while retaining others [16]. PIM-1 can exhibit very high sorption selectivity. For example, in sorption from ethanolic solution of the neutral dye Solvent Blue 35 (also known as Sudan Blue II), the dye concentration within the membrane was more than three orders of magnitude higher than in the surrounding ethanol solution, representing a much higher affinity than achieved with two other high free volume polymers, poly(1-trimethylsilyl-1-propyne) (PTMSP) and poly(4-methyl-2-pentyne) (PMP) [17]. The possibility has been demonstrated of utilising PIM-1 both as an adsorbent and as a membrane material, in a combined process of solvent swing adsorption with solvent recovery by nanofiltration [18].

Chemical modification of PIM-1 (Fig. 1) has been employed to tailor its selectivity for both gas and liquid phase separations. The nitrile groups in PIM-1 may be hydrolysed to a mixture of amide and carboxylated functional groups [19,22,23], and it has been shown that adsorption from aqueous solution of a cationic dye (Safranin O) increases dramatically with increasing degree of carboxylation, while uptake of an anionic dye (Orange II) decreases [19]. Chemical modification of PIM-1 with ethanolamine or diethanolamine has been shown to yield predominately hydroxyalkylaminoalkylamide structures [20], and these products exhibit the opposite dye adsorption behaviour to hydrolysed PIM-1, being selective for the anionic, rather than the cationic dye. The nitrile groups in PIM-1 may also be converted to a variety of other chemical structures, including thioamide [24], tetrazole [25], methyl tetrazole [26], amidoxime [27,28] and amine [21]. The present contribution provides additional data on adsorption of a range of dyes (Fig. 2) by hydrolysed and ethanolamine-modified PIM-1 powder samples, along with comparative data for amine-PIM-1, which has not previously been studied in this way. The effects of pH and temperature are discussed. Selective adsorption is demonstrated with mixtures of dyes for the first time.

The properties of PIM-1 may also be modified through ultraviolet [29–31] or thermal [32,33] treatment. Thermal treatment of chemically modified polymers may bring about the loss of chemical functionality. Thermal treatment of hydrolysed PIM-1 under an inert atmosphere has been shown to give crosslinked products, possibly through a decarboxylation-induced process [34]. The present contribution considers the effect of thermal treatment on hydrolysed PIM-1, ethanolamine-modified PIM-1, diethanolamine-modified PIM-1 and amine-PIM-1 samples, and utilises dye adsorption to demonstrate the resulting dramatic change in properties.

2. Experimental

2.1. Materials

Dimethylacetamide (DMAc), toluene, methanol (MeOH), sodium hydroxide, chloroform, Safranin O (>85% dye content), Methylene Blue Hydrate (⩾97.0%), Orange II Sodium Salt (>85%

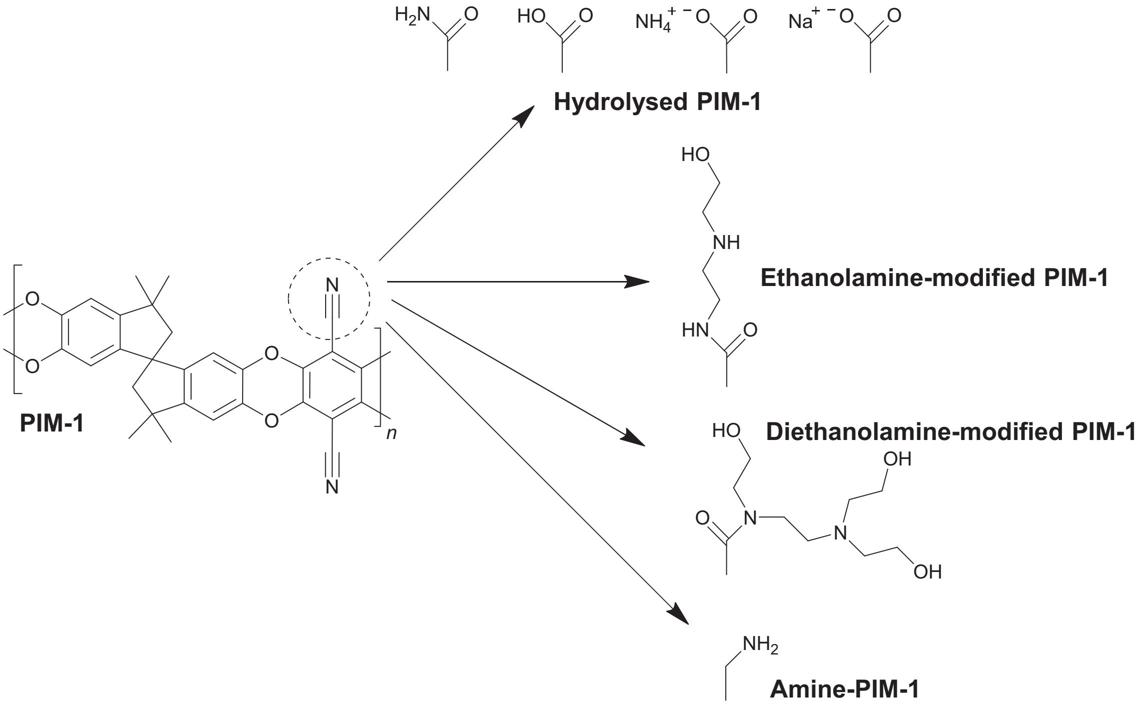

Fig. 1. Chemical structure of the polymer of intrinsic microporosity PIM-1 and structures formed by base-catalysed hydrolysis [19], by ethanolamine and diethanolamine modification [20], and on reduction to amine [21].

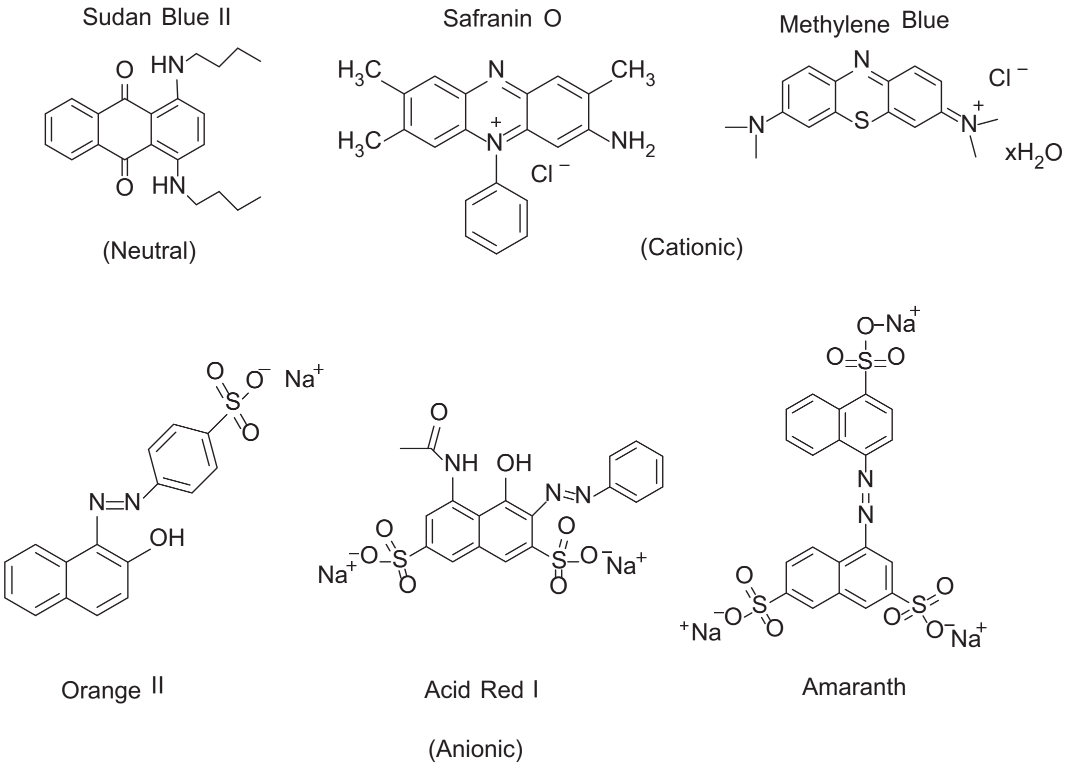

Fig. 2. Chemical structures of dyes used in the present study.

dye content), Acid Red I, Amaranth, Sudan Blue II (98%), ethanolamine (purified by redistillation, ⩾99.5%), diethanolamine (reagent grade, ⩾98.0%) and borane dimethyl sulfide complex (5 M in diethyl ether) were purchased from Sigma-Aldrich and used as received. Tetrafluoroterephthalonitrile (TFTN, 98%, Aldrich) was purified by sublimation; it was heated to around 150 °C and the pure product collected without vacuum. 5,5′,6,6′-Tetrahydroxy-3,3,3′,3′-tetramethyl-1,1′-spirobisindane (THSBI, 98%, Alfa Aesar) was dissolved in methanol and re-precipitated from dichloromethane before use. Anhydrous potassium carbonate (K_2CO_3, 99.0%, Fisher) was dried in an oven at 110 °C overnight before use.

2.2. Characterization methods

Infrared (IR) spectra were recorded with a resolution of 0.5 cm^{-1} on a Thermo Scientific™ Nicolet iS5 FT-IR Spectrometer with an Attenuated Total Reflectance (ATR) accessory.

^{1}H Nuclear magnetic resonance (NMR) spectra were recorded using a Bruker Avance II 500 MHz NMR spectrometer at room temperature. Polymer solutions for NMR were prepared in $CDCl_3$ or DMSO and left to stir overnight. Signal peaks for solvents were used as references.

High powered decoupling (Hpdec) magic angle spinning (MAS) solid state ^{13}C NMR spectra were collected using a Bruker Avance III 400 MHz instrument. Adamantane was used as a reference and 10,000 Hz spinning rate was used with powder and membrane samples packed into a 4 mm zirconium rotor. Spectra were compiled from 6000 scans using a repetition time of 10 s and a spectral width of 600 ppm.

Elemental analysis was carried out by the School of Chemistry Microanalysis Service, University of Manchester, using a Thermo Scientific Flash 2000 organic elemental analyzer (CHNS analyzer). For chlorine analysis, the sample was accurately weighed and then combusted using a Schöniger flask procedure (oxygen flask). The gas products were absorbed into aqueous solution which was then titrated using silver nitrate. An autotitrator was used (Metrohm 888 Titrando), programmed to calculate the % chlorine in the sample. For Na analysis, the sample was accurately weighed and transferred to a glass digestion tube. Concentrated acid was added (mixture of nitric, perchloric and sulphuric acid) and the tube was heated to around 320 °C to digest the sample. After cooling the remaining solution was diluted and transferred to a volumetric flask. The concentration of sodium in the solution was then measured using an ICP-OES instrument (Thermo Scientific iCAP 6300Duo).

Thermogravimetric Analysis (TGA) was carried out using a Mettler Toledo Star System. Polymer samples were heated to 600 °C at 10 °C min^{-1} under a nitrogen atmosphere.

Average molar masses of polymers were determined by multi-detector gel permeation chromatography (GPC), using a Viscotek VE2001 GPC solvent/sample module with two PL Mixed B columns and a Viscotek TDA302 triple detector array (refractive index, light scattering, viscosity detectors). Analysis was performed in $CHCl_3$ at a flow rate of 1 mL min^{-1}. Data were analysed by the OmnicSec program.

2.3. Synthesis of PIM-1

Two batches of PIM-1 were utilised in the current work, denoted BPIM and TPIM. Both batches were synthesised by the method of Du et al. [35].

For batch BPIM, all glassware was washed with acetone before use and dried in an oven overnight at 110 °C. Under a stream of dry N_2 gas, a mixture of THSBI (34.04 g, 0.1 mol), TFTN (20.01 g, 0.1 mol), anhydrous K_2CO_3 (41.4 g, 0.3 mol), DMAc (200 mL), and toluene (100 mL) were added to a 2 L flask, which was then equipped with mechanical stirrer, Dean-Stark trap and reflux condenser. The mixture was heated at 160 °C for 40 min. The viscous solution was dissolved in chloroform and re-precipitated from methanol. The polymer was refluxed overnight with deionized water and dried at 110 °C in a vacuum oven for 48 h. GPC: M_n = 49,000 g mol^{-1}, M_w = 157,000 g mol^{-1}, M_w/M_n = 3.2. ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 6.75 (2H, s), 6.35 (2H, s), 2.26–2.09 (4H, dd), 1.40–1.10 (broad, 12H). ATR-IR (cm^{-1}): 2995, 2864, 2239, 1605, 1446, 1264. Anal. calcd for $C_{29}H_{20}N_2O_4$ (wt%): C: 75.64, H: 4.37, N: 6.08 Found: C: 73.6, H: 4.4, N: 5.96.

For batch TPIM, the procedure was the same, but the quantities were half those given above. GPC: M_n = 34,000 g mol^{-1}, M_w = 99,000 g mol^{-1}, M_w/M_n = 2.9. ^{1}H NMR and ATR-IR as above. Anal. Found: C: 74.2, H: 3.4, N: 6.1.

2.4. Chemical modification of PIM-1

The hydrolysis of PIM-1 has been described previously [19]. Three samples from the previous study were used: AMD7, ACD21 and ACD23, hydrolysed 89%, 96% and 98%, respectively, and carboxylated 11%, 37% and 51%, respectively.

A fresh sample of hydrolysed PIM-1 (ACD) was prepared for studies of thermal treatment. TPIM powder (0.9 g) was stirred in 20% NaOH solution (H_2O/EtOH 1/1) at 120 °C for 24 h. The product was washed as described previously [19]. Characterization data are provided in supplementary information.

Ethanolamine modification of PIM-1 was carried out as described previously [20]. For sample EAP6, BPIM powder (0.8 g) was put into a three neck flask under an inert atmosphere of nitrogen. Ethanolamine (10 mL) was added and the reaction set to 120 °C under a reflux condenser. After 20 h, polymer was isolated by pouring into ethanol (100 mL) and washed with distilled water (200 mL). The sample was dried in a vacuum oven at 110 °C overnight. Anal. Found wt%: C: 65.86, H: 5.4, N: 7.99. Calculated fraction modified, x_{mod} = 0.87 (using method described in [20]). Further characterization data are provided in supplementary information.

For ethanolamine-modified PIM-1 sample EAP, used for thermal treatment, TPIM powder (1.2 g) was stirred in 29 ml ethanolamine solution at 120 °C for 30 h under an atmosphere of nitrogen. Characterization data are provided in supplementary information.

Diethanolamine modification of PIM-1 (sample DEA) was carried out as described previously [20]. TPIM powder (0.9 g) was stirred in 15 g diethanolamine solution at 150 °C for 24 h under an atmosphere of nitrogen. Characterization data are provided in supplementary information.

Amine modification of PIM-1 was carried out as described previously [21]. PIM-1 (BPIM, 2.50 g) was reduced by 5.0 M borane-dimethyl sulfide complex in diethyl ether (60 mL, 285 mmol), The reaction was set to reflux overnight with constant stirring, After cooling, ethanol (400 mL) was added dropwise to remove excess borane. The solid was collected and stirred overnight in 1.0 M methanolic HCl (400 mL), then separated by vacuum filtration and stirred in 5% aqueous NaOH solution (800 mL) overnight. The solid (sample AM10) was washed repeatedly with water until neutral and dried at 110 °C under vacuum overnight. Yield: 2.38 mg (96%). Found wt%: C: 71.4, H: 6.1, N: 5.5. Further characterization data are provided in supplementary information.

2.5. Dye adsorption

Dye concentrations were determined by UV spectroscopy. UV spectra were obtained with a wavelength resolution of 1 nm using a Shimadzu UV-1800 spectrometer, which has a photometric range of −4 to 4 Abs. Structures of the dyes employed are given in Fig. 2. Two dyes were used for studies of dye adsorption from ethanolic solution, the anionic dye Orange II Sodium salt (molecular formula $C_{16}H_{11}N_2NaO_4S$, molecular weight: 350.32) and the neutral dye Sudan Blue II (molecular formula $C_{22}H_{26}N_2O_2$, molecular weight: 350.45). Five dyes were used for studies of dye adsorption from aqueous solution, three anionic dyes, Orange II Sodium salt, Acid Red I (molecular formula $C_{18}H_{13}N_3Na_2O_8S_2$, molecular weight: 509.42) and Amaranth (molecular formula $C_{20}H_{11}N_2Na_3O_{10}S_3$, molecular weight: 604.47), and two cationic dyes, Safranin O (molecular formula $C_{20}H_{19}ClN_4$, molecular weight: 350.84) and Methylene Blue Hydrate (molecular formula $C_{16}H_{18}ClN_3S{\cdot}xH_2O$, anhydrous molecular weight 319.85), Stock solutions were prepared and diluted to give calibration solutions with concentrations in the range 50–0.39 mg L^{-1}. Aqueous solutions were prepared with deionized water. Values determined for the specific adsorption coefficient, *a*, for each dye are given in Table 1.

Oven-dried adsorbent (~3.0–10.0 mg) was placed in 50–100 mL of 50 ppm dye solution. For experiments in aqueous solution at different pH, 1 M HCl or NaOH were used to adjust the pH of the dye solution. The dye solution containing the adsorbent was stirred well with a magnetic stirrer for 24–72 h, after which time there was little further uptake of dye. 3 mL aliquots were taken periodically by syringe and filtered through a PTFE hydrophobic filter (0.45 μm). The mass of dye adsorbed by the polymer, q_e (mg g^{-1}), was determined from the absorbance of the dye solution before contact with polymer, A_0, and the absorbance of the dye solution after reaching effective equilibrium with the polymer, A_e, using Eq. (1).

$$q_e = \frac{(A_0 - A_e)V}{alm} \qquad (1)$$

where *V* is the total volume of dye solution, *a* is the specific absorption coefficient, *l* is the path length in the spectrometer and *m* is the total mass of polymer.

For dye adsorption studies of a binary mixture, a Methylene Blue solution (50 mL, 25 mg L^{-1}) was mixed with an Orange II (50 mL, 50 mg L^{-1}) solution. An amount of oven-dried adsorbent (~5.0 mg) was placed in the mixture (100 mL) and stirred for 72 h.

2.6. Thermal treatment

PIM-1 (batch TPIM) and chemically modified polymers were thermally treated using a Carbolite 1200 °C Three Zone tube furnace. The furnace temperature was raised to 300 °C at a rate of 10 °C min^{-1} and held for a period of 48 h under a steady flow of nitrogen. After the thermal treatment, polymers were allowed to cool in the furnace to room temperature.

3. Results and discussion

3.1. Dye adsorption from ethanolic solution

It was previously shown for a membrane sample that PIM-1 exhibits very high adsorption of a neutral dye from ethanolic solution [17]. This is confirmed by the results in Table 2 for dye adsorption from ethanolic solution by powder samples. PIM-1 shows high uptake of the neutral dye Sudan Blue II, whereas the value obtained for q_e for the anionic dye Orange II is negative. PIM-1 is known to swell in ethanol [36], and the negative value of q_e may be attributed to preferential uptake of ethanol, leading to concentration of dye in the surrounding solution. The strong affinity of PIM-1 for the neutral dye is lost on chemical modification, with hydrolysed, ethanolamine-modified and amine-PIM-1 samples all showing negative values of q_e for Sudan Blue II. Conversion of the nitrile in PIM-1 to a primary amine led to increased affinity for the anionic dye. Further studies of dye adsorption were carried out from aqueous solution, as discussed below.

Table 1
Values of absorption maximum, λ_{max}, and specific adsorption coefficient, *a*, for dyes in ethanolic and in aqueous solution.

Dye	Ethanolic solution		Aqueous solution	
	λ_{max} (nm)	a (L mg^{-1} cm^{-1})	λ_{max} (nm)	a (L mg^{-1} cm^{-1})
Orange II	481	0.0502	484	0.0597
Sudan Blue	644	0.0312	–	–
Safranin O	–	–	509	0.0893
Methylene Blue	–	–	665	0.1567
Acid Red I	–	–	531	0.0394
Amaranth	–	–	521	0.0381

Table 2
Apparent adsorption of a neutral dye and an anionic dye from ethanolic solution by PIM-1 and chemically modified PIM-1 powder samples at ambient temperature (*ca.* 20 °C).

Polymer	Batch	q_e (mg g^{-1})	
		Sudan Blue II (neutral)	Orange II (anionic)
PIM-1	BPIM	94	−14
Hydrolysed PIM-1 (11% carboxylated)	AMD7	−4	–
Hydrolysed PIM-1 (37% carboxylated)	ACD21	−13	−11
Ethanolamine-modified PIM-1	EAP6	−5	–
Amine-PIM-1	AM10	−5	−1

3.2. Single dye adsorption from aqueous solution

Values of q_e are given in Table 3 for adsorption from aqueous solution of two cationic dyes and three anionic dyes at ambient temperature. For hydrolysed PIM-1, the previously reported [19] increase in adsorption of the cationic dye Safranin O with increasing degree of carboxylation is confirmed for another cationic dye (Methylene Blue). The selectivity for cationic over anionic dyes is also confirmed. Similarly, for ethanolamine-modified PIM-1, the previously reported [20] reverse selectivity for anionic over cationic dyes is confirmed. It can also be seen from Table 3 that amine-PIM-1, like ethanolamine-modified PIM-1, shows selectivity for anionic over cationic dyes.

The uptake of organic compounds by a PIM is a complex process, which may be thought of in terms of adsorption on the internal surface and/or dissolution in the polymeric matrix. The significance of "microporosity" is that adsorption is enhanced through multi-wall interactions. A variety of intermolecular forces may contribute to interactions between a penetrant and the polymer, including pi-pi interactions between aromatic groups, dipole-dipole interactions and, for ionic species, charge-charge and charge-dipole interactions. For ionic dyes, as studied here, charge interactions may be assumed to dominate the selectivity, cationic species being taken up by, and anionic species rejected by, polymers that bear an effective negative charge, and the reverse being the case for polymers that bear an effective positive charge. This effect is expected to be strongest under conditions for which there is a high degree of ionization of the polymer, *i.e.* at high pH for hydrolysed PIM-1, and at low pH for amine-containing polymers.

The effect of pH on dye adsorption is shown in Fig. 3. For hydrolysed PIM-1 (Fig. 3(a)) there is, as expected, a decrease in the uptake of cationic dyes at low pH, when the acid groups are neutralised. For the basic adsorbents, amine-PIM-1 and ethanolamine-modified PIM-1 (Fig. 3(b)), there is a substantial increase in adsorption of anionic dyes at low pH, when the amine groups are protonated. At low pH, the amine-PIM-1 took up more than its own weight of Orange II and Acid Red I. Only a few adsorbents, such as cross-linked chitosan beads [37], have been reported to give higher adsorption capacities. PIMs offer the advantages of tailorability and the potential to be applied in membrane processes.

A potential disadvantage of a purely microporous material such as a PIM, as a solid-state adsorbent, is slow kinetics. More rapid adsorption was observed for cationic dyes by hydrolysed PIM-1, which reached maximum uptake within 24 h, than for anionic dyes by ethanolamine-modified PIM-1 and amine-PIM-1, which required 72 h. Adsorption was studied over time and first and second order kinetic models were applied (see supplementary information). The models could not be distinguished within the precision of the data, but the results confirm the more rapid adsorption by hydrolysed PIM-1.

3.3. Mixed dye adsorption from aqueous solution

The single dye adsorption data indicated that hydrolysed PIM-1 shows selectivity for cationic dyes over anionic dyes, whereas ethanolamine-modified PIM-1 and amine-PIM-1 show selectivity for anionic dyes over cationic dyes. Adsorption from a mixture of Methylene Blue and Orange II was conducted to provide a convincing demonstration of this selectivity. Experiments with mixtures of cationic and anionic dyes are complicated by precipitation that occurs on mixing the oppositely charged species. Nevertheless, preferential adsorption of one species leads to dissolution of the other from the precipitate, so the selectivity may be demonstrated by colour changes in the solution, as can be seen in Fig. 4. A solution of Methylene Blue is a strong blue colour, and of Orange II is a strong orange colour, but the mixture, after filtering out the precip-

Table 3
Adsorption of cationic and anionic dyes from aqueous solution by PIM-1 and chemically modified PIM-1 powder samples at ambient temperature (*ca.* 20 °C).

Polymer	Batch	q_e (mg g^{-1})				
		Cationic dyes		Anionic dyes		
		Safranin O	Methylene Blue	Orange II	Acid Red I	Amaranth
PIM-1	BPIM	15	4	11	2	5
Hydrolysed PIM-1 (11% carboxylated)	AMD7	100	47	33	−4	0
Hydrolysed PIM-1 (37% carboxylated)	ACD21	215	175	21	1	1
Hydrolysed PIM-1 (51% carboxylated)	ACD23	467	285	4	–	–
Ethanolamine-modified PIM-1	EAP6	43	5	425	525	325
Amine-PIM-1	AM10	36	8	275	393	135

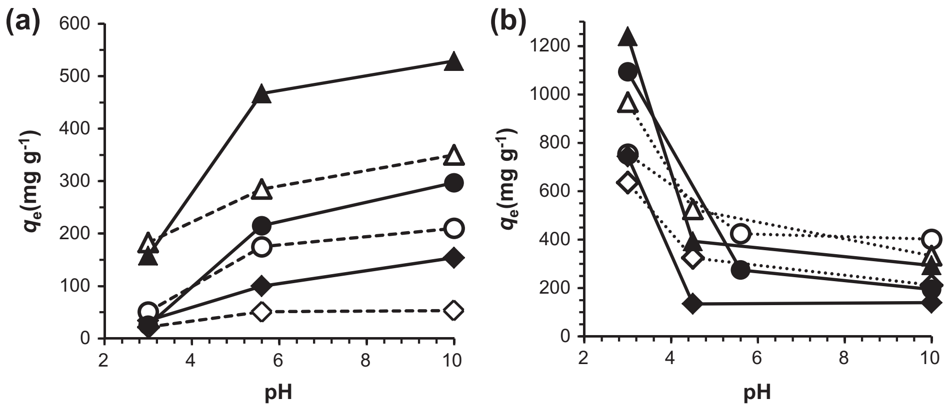

Fig. 3. The effect of pH on the adsorption of (a) cationic dyes Safranin O (filled symbols, solid lines) and Methylene Blue (open symbols, dashed lines) by hydrolysed PIM-1 with degrees of carboxylation of 11% (◆, ◇), 37% (●, ○) and 51% (▲, △), and (b) anionic dyes Orange II (●, ○), Acid Red I (▲, △) and Amaranth (◆, ◇) by amine-PIM-1 (filled symbols, solid lines) and ethanolamine-modified PIM-1 (open symbols, dashed lines).

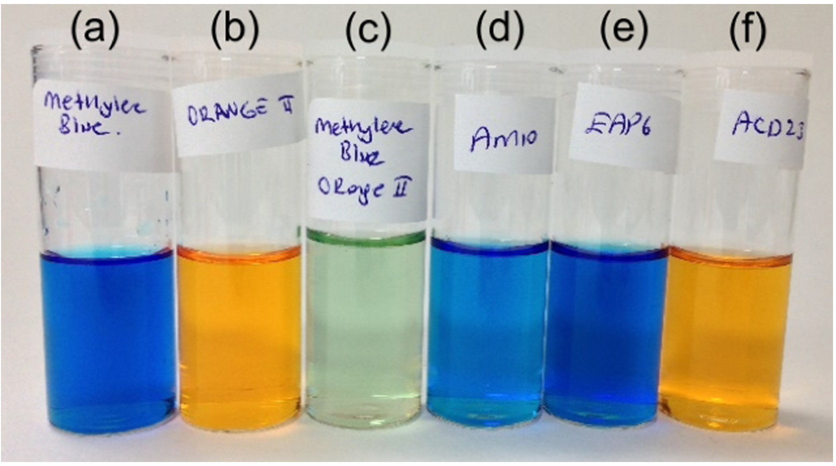

Fig. 4. Filtered solutions of (a) Methylene Blue, (b) Orange II, (c) mixture of Methylene Blue and Orange II before contact with adsorbent, and mixture after contact with (d) amine-PIM-1, (e) ethanolamine-modified PIM-1 and (f) hydrolysed PIM-1.

itate, is weak in colour, because most of the dye is in the precipitate. However, contact with amine-PIM-1 or ethanolamine-modified PIM-1 leads to a blue solution, due to dissolution of the blue dye as the orange is adsorbed, while contact with hydrolysed PIM-1 leads to an orange solution, due to dissolution of the orange dye as the blue is adsorbed. This effect is further shown by UV–visible spectroscopy (see supplementary information).

For a practical adsorption process, it must also be demonstrated that dye can be desorbed and the adsorbent regenerated. Fig. 5 demonstrates desorption of Orange II from amine-PIM-1 using ethanol to which a few drops 1 M NaOH have been added.

3.4. Thermal treatment of chemically modified PIM-1

Chemical modification may be used to tailor the adsorption behaviour of a PIM, but it may also reduce the thermal stability compared to the parent polymer. Thermogravimetric analysis (TGA) of samples of hydrolysed PIM-1, ethanolamine-modified PIM-1, diethanolamine-modified PIM-1 and amine-PIM-1 are shown in Fig. 6, before and after thermal treatment at 300 °C for 48 h under nitrogen. The parent PIM-1 (Fig. 6(a)) shows no significant degradation below 450 °C under the conditions of a TGA experiment. The chemically modified PIMs undergo significant weight losses at lower temperatures than the parent polymer. Weight losses at moderate temperature (<150 °C) may be attribu-

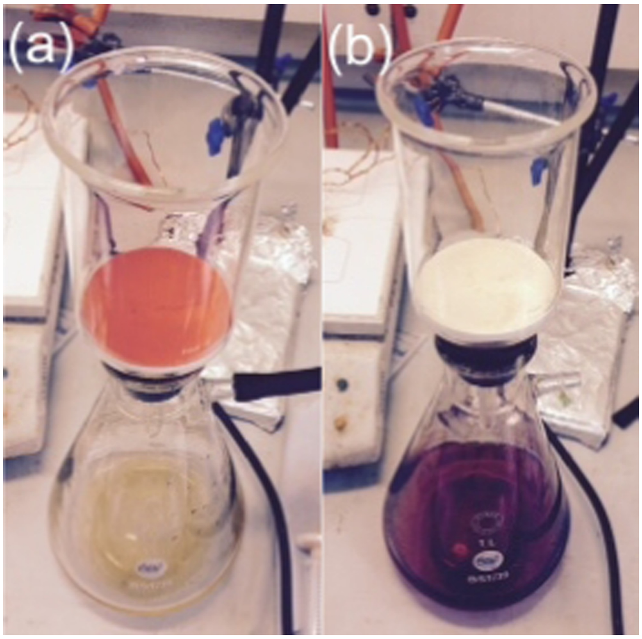

Fig. 5. Illustration of desorption of Orange II from amine-PIM-1 powder by basic ethanol (a) amine-PIM-1 powder with adsorbed Orange II on funnel, (b) concentrated ethanolic dye solution in flask and light yellow adsorbent retained on funnel.

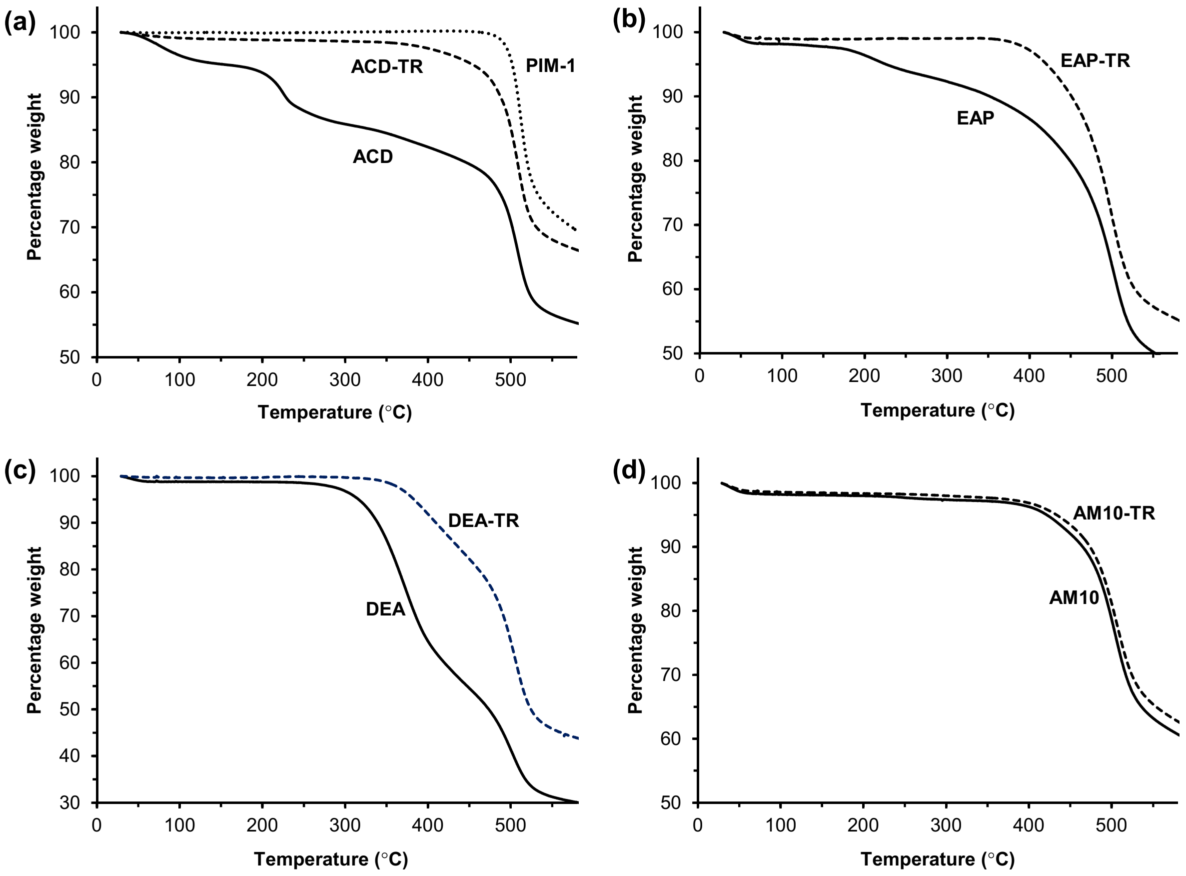

Fig. 6. Thermogravimetric analysis (TGA) before (solid lines) and after (dashed lines) thermal treatment for (a) hydrolysed PIM-1, (b) ethanolamine-modified PIM-1, (c) diethanolamine-modified PIM-1 and (d) amine-PIM-1. TGA of the parent PIM-1 is included as a dotted line in (a).

ted to loss of adsorbed vapours or residual solvents. Weight losses at intermediate temperature (150–400 °C) suggest structural changes, such as loss of functional groups. For thermally treated polymers, the intermediate weight losses are not observed in TGA, because those structural changes occurred during the thermal treatment. Weight losses at higher temperature (>400 °C) are associated with degradation of the polymer backbone.

The weight losses at intermediate temperature can be used to determine the fraction of polymer mass that remains after thermal treatment. Hence, the effective molar mass of a repeat unit in the thermally-treated polymer, $M_{r,t}$, can be calculated using Eq. (2)

$$M_{r,t} = \frac{W_u}{W_t} M_{r,u} \qquad (2)$$

where W_u and W_t are the percentage weights of the untreated and thermally treated polymer, respectively, remaining at 400 °C in a TGA experiment, after correction for low temperature (<150 °C) weight losses due to adsorbed vapours or residual solvents, and $M_{r,u}$ is the effective molar mass of a repeat unit of the untreated polymer. The effective molar mass of a repeat unit is an average for the different structures which may be present in the polymer. The value of $M_{r,u}$ for each modified PIM-1 can be calculated on the basis of compositional analysis appropriate for each modification, as discussed in supplementary information.

The thermally treated polymers were insoluble in common solvents, so characterization was limited to elemental analysis, attenuated total reflection infra-red (ATR-IR) spectroscopy and solid-state NMR spectroscopy. Elemental analysis results for untreated

Table 4
Weight percentage of elements from elemental analysis, percentage weight of polymer at 400 °C in TGA, corrected for low temperature weight losses (W_p), effective molar mass of a repeat unit (M_r), empirical formula for the repeat unit, molar mass of repeat unit with the empirical formula ($M_{r,e}$), Scaling factor (S), and effective formula of the repeat unit, for hydrolysed PIM-1 before (ACD) and after (ACD-TR) thermal treatment, ethanolamine-modified PIM-1 before (EAP) and after (EAP-TR) thermal treatment, diethanolamine-modified PIM-1 before (DEA) and after (DEA-TR) thermal treatment and amine-PIM-1 before (AM10) and after (AM10-TR) thermal treatment.

Polymer	Elemental analysis (wt%)					W_p	M_r	Empirical formula of repeat unit					$M_{r,e}$	S	Effective formula of repeat unit				
	C	H	N	O	Na			C	H	N	O	Na			C	H	N	O	Na
ACD	61.1	4.9	2.6	30.1	1.3	86.6	509.9	90.0	86.0	3.3	33.3	1.0	1768.5	0.29	25.9	24.8	0.9	9.6	0.3
ACD-TR	71.5	5.0	2.3	19.7	1.6	98.5	448.3[a]	87.7	72.4	2.4	18.2	1.0	1473.7	0.30	26.7	22.0	0.7	5.5	0.3
EAP	66.4	5.47	7.82	20.3	0	88.5	624.1	9.9	9.7	1.0	2.3	0.0	179.1	3.48	34.5	33.9	3.5	7.9	0.0
EAP-TR	69.9	4.83	6.21	19.1	0	98.3	562.3	13.1	10.8	1.0	2.7	0.0	225.6	2.49	32.7	26.9	2.5	6.7	0.0
DEA	62.2	6.9	6.2	24.7	0	65.4	761.1	11.7	15.5	1.0	3.5	0.0	225.9	3.37	39.4	52.1	3.4	11.8	0.0
DEA-TR	72.6	6	3.9	17.6	0	91.6	543.4	21.7	21.4	1.0	4.0	0.0	359.5	1.51	32.8	32.3	1.5	6.0	0.0
AM10	71.4	6.1	5.5	17	0	96.3	470.6	15.1	15.4	1.0	2.7	0.0	254.7	1.85	28.0	28.5	1.8	5.0	0.0
AM10-TR	71.2	5	4.1	19.7	0	96.9	467.7	20.3	16.9	1.0	4.2	0.0	341.6	1.37	27.7	23.2	1.4	5.8	0.0

[a] Contains a small amount of salt.

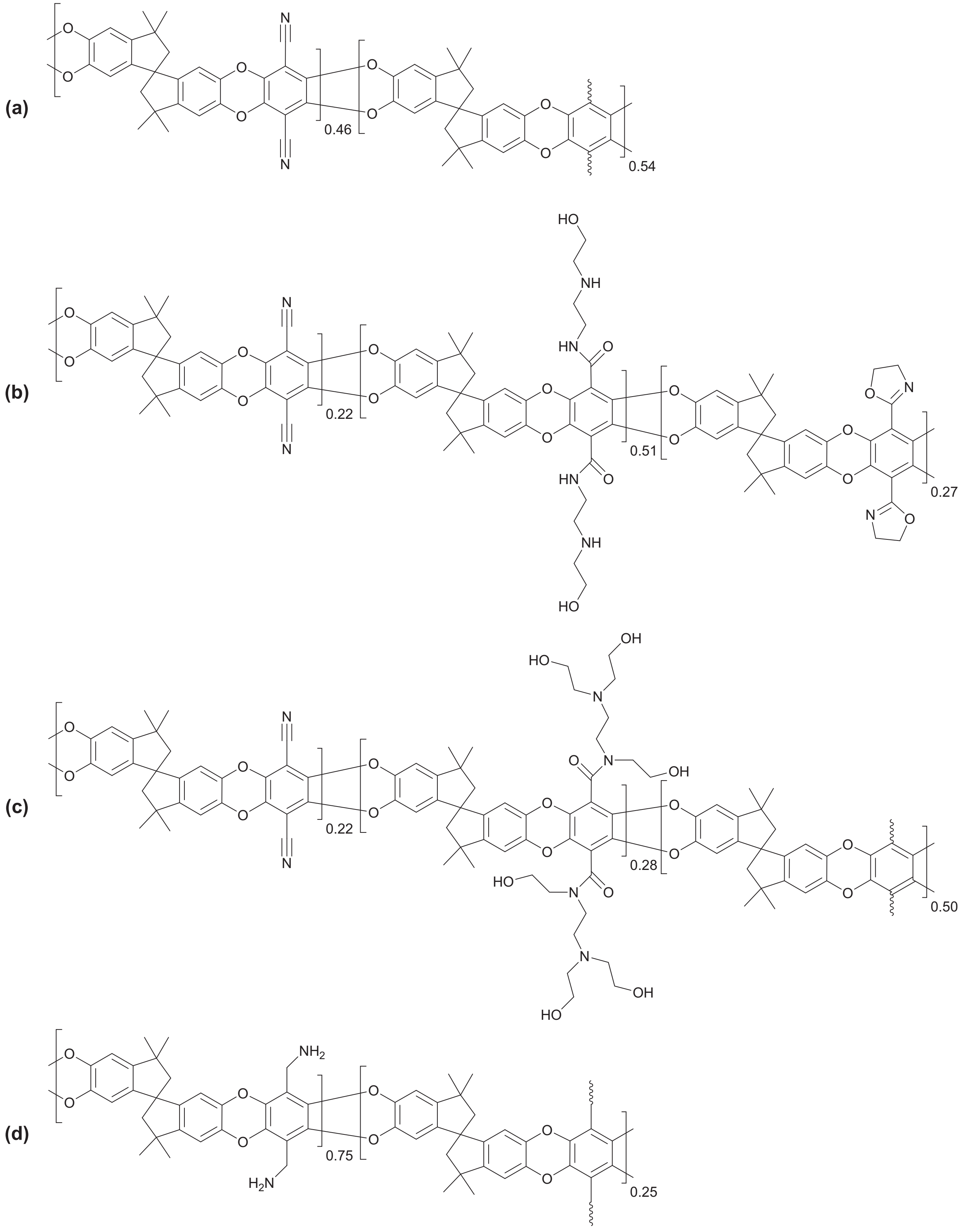

Fig. 7. Feasible structures for the products of thermal treatment of (a) hydrolysed PIM-1 (ACD-TR), (b) ethanolamine-modified PIM-1 (EAP-TR), (c) diethanolamine-modified PIM-1 (DEA-TR), and (d) amine-PIM-1 (AM10-TR). Wavy lines indicate possible crosslinking sites. Numbers indicate mole fractions of the idealised repeat unit; in reality repeat units may have mixed functionality.

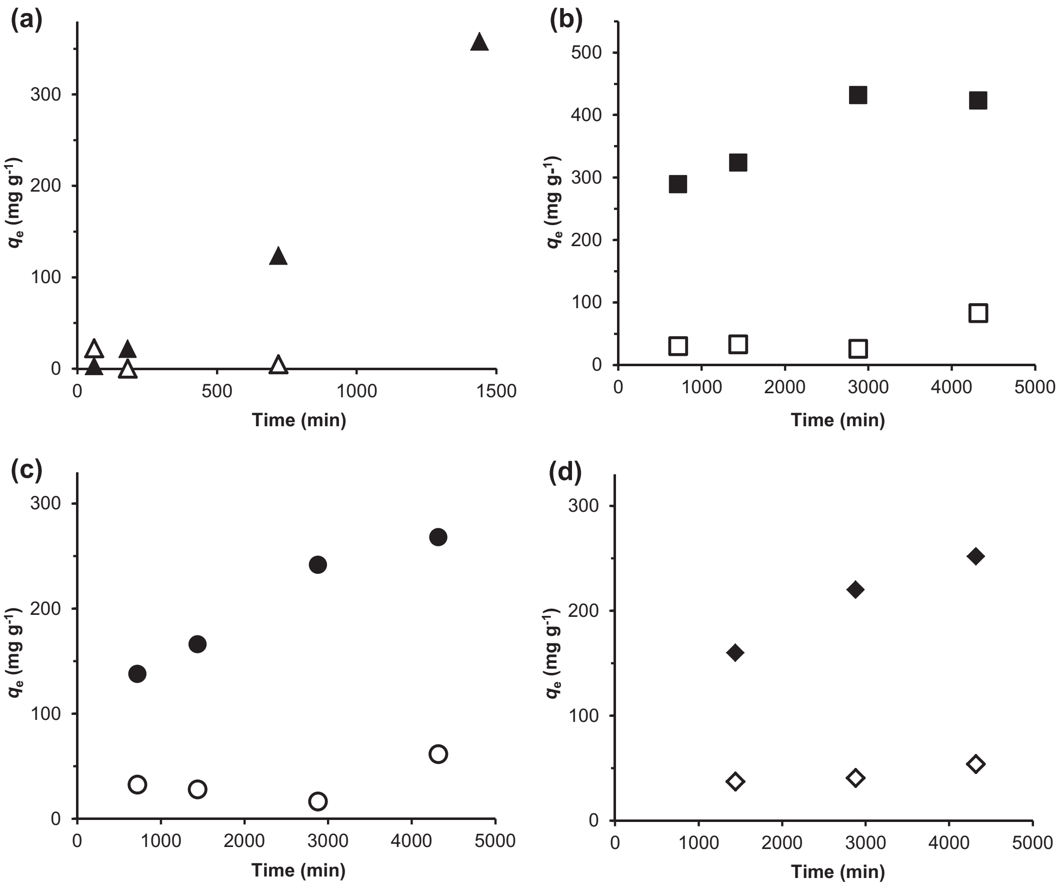

Fig. 8. Amount of dye adsorbed as a function of time for chemically modified polymers before (filled symbols) and after (open symbols) thermal treatment: (a) hydrolysed PIM-1 with Safranin O, (b) ethanolamine-modified PIM-1 with Orange II, (c) diethanolamine-modified PIM-1 with Orange II, and (b) amine-PIM-1 with Orange II.

and thermally treated polymers are given in Table 4. These data, together with values of $M_{r,u}$ and $M_{r,t}$ obtained as indicated above, can be used to determine the effective formula of a repeat unit. The number of moles, n_X, of element X are calculated from the weight percentage, w_X, of that element, determined by elemental analysis, and its molar mass, M_X, using Eq. (3).

$$n_X = \frac{w_X}{M_X} \tag{3}$$

The empirical formula for the repeat unit is thus obtained by dividing n_X for each element by the value for the element present in smallest amount, $n_{X,min}$. Hence, the molar mass $M_{r,e}$ corresponding to a repeat unit with the empirical formula is determined using Eq. (4).

$$M_{r,e} = \sum \frac{n_X}{n_{X,min}} M_X \tag{4}$$

Scaling factors, S_u and S_t, are calculated for the untreated and thermally treated polymers, respectively, using

$$S_u = \frac{M_{r,u}}{M_{r,eu}} \text{ and } S_t = \frac{M_{r,t}}{M_{r,et}} \tag{5}$$

where $M_{r,eu}$ and $M_{r,et}$ are the empirical formulae determined using Eq. (4) for the untreated and thermally treated polymer, respectively. Thus, the amount of each element, $n_{X,u}$ and $n_{X,t}$, in repeat units of molar mass $M_{r,u}$ and $M_{r,t}$, respectively, are determined as

$$n_{X,u} = \frac{n_X}{n_{X,min}} S_u \text{ and } n_{X,t} = \frac{n_X}{n_{X,min}} S_t \tag{6}$$

Effective formulae of the repeat units of untreated and thermally treated polymers, determined using this approach, are included in Table 4.

On the basis of this analysis, and the further characterization provided in supplementary information, feasible structures for the thermally treated polymers can be suggested, as indicated in Fig. 7.

Hydrolysed PIM-1 is believed to contain a mixture of amide, carboxylic acid, ammonium carboxylate and sodium carboxylate structures, along with a small amount of residual nitrile. On thermal treatment, it is likely that amide releases water to regenerate a nitrile structure, that carboxylic acid decomposes with loss of CO_2, that ammonium carboxylate releases ammonia to form carboxylic acid, which then either further decomposes with loss of CO_2 or reacts with ammonia to give amide and thence nitrile, and that sodium carboxylate decomposes to generate a sodium salt, probably Na_2CO_3. Thus, the thermally treated polymer most likely contains a mixture of nitrile and unfunctionalised or crosslinked structures (Fig. 7(a)), with a little trapped salt.

Ethanolamine-modified PIM-1 is believed to have a hydroxyethylaminoethylamide structure, along with some residual nitrile. On thermal treatment, it is likely that a proportion of the hydroxyethylaminoethylamide is converted to an oxazoline structure, so that the thermally treated polymer contains a mixture of nitrile, hydroxyethylaminoethylamide and oxazoline functionality (Fig. 7(b)).

Diethanolamine-modified PIM-1 is believed to form a hydroxyalkylaminoalkylamide structure from addition of two diethanolamine per nitrile, along with some residual nitrile. On thermal treatment it is likely that much of the hydroxyalkylaminoalkylamide is lost, giving unfunctionalised or crosslinked structures (Fig. 7(c)).

Amine-PIM-1 loses some nitrogen on thermal treatment, presumably as ammonia, so the thermally treated polymer most likely contains a mixture of amine and unfunctionalised or crosslinked structures (Fig. 7(d)).

The effect of thermal treatment on the dye adsorption behaviour is illustrated in Fig. 8. In each case, there is a loss of capacity for a dye which is strongly adsorbed by the untreated polymer. It is particularly noteworthy that thermal treatment of amine-PIM-1 dramatically reduces its dye adsorption, although the evidence suggests only a quarter of the amine functionality is lost on thermal treatment. This is most likely a consequence of crosslinking and loss of internal porosity.

4. Conclusions

This research has realised its aim of developing materials capable of the selective uptake of organic species from aqueous or other media. This is relevant to the recovery of high value products in the fine chemicals industry and to specialised processes for wastewater treatment.

Chemical modification of the polymer of intrinsic microporosity PIM-1 enables polymers to be prepared with tailored sorption selectivity, as demonstrated by single and mixed dye adsorption experiments. Amine-PIM-1, ethanolamine-modified PIM-1 and diethanolamine-modified PIM-1 exhibit selectivity for anionic over cationic species, with very high capacity being achieved at low pH. Amine-PIM-1 is able to take up more than its own weight of Orange II and Acid Red I at low pH, outperforming most adsorbents reported in the literature.

The reverse selectivity, for cationic over anionic species, is achieved with hydrolysed PIM-1. However, thermal treatment of chemically modified polymers at 300 °C in an inert atmosphere leads to a loss of functionality, possibly coupled with crosslinking, that reduces the dye adsorption capacity.

These polymers show potential as selective media for both solvent-swing adsorption and membrane processes [18]. Further research will seek to extend the range of selective materials, and to optimise them for practical application in separation processes.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcis.2016.12.048.

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