



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.

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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 adsorbents 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 O₂/N₂, CO₂/CH₄ and CO₂/N₂ [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%

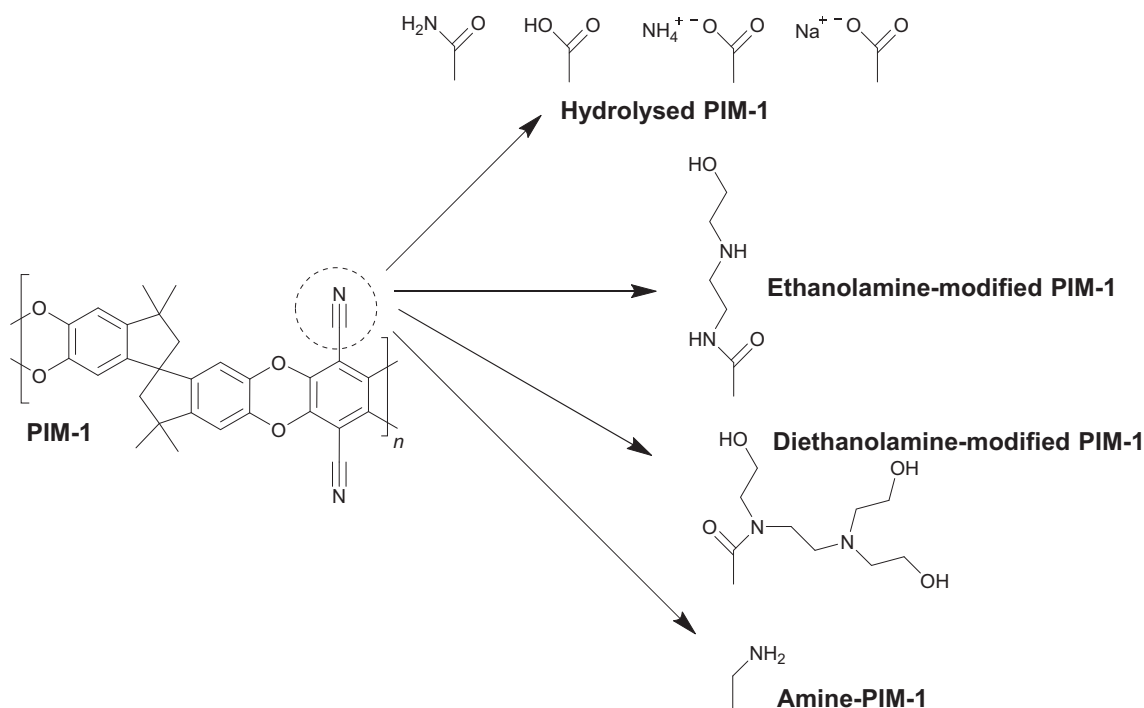


Fig. 1. Chemical structure of the polymer of intrinsic microporosity PIM-1 and structures formed by base-catalysed hydrolysis [19], by ethanolamine and diethanolamine modification [20], and on reduction to amine [21].

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