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Research article

Conversion of post consumer waste polystyrene into a high value adsorbent and its sorptive properties for Congo Red removal from aqueous solution

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ABSTRACT

Using post-consumer waste polystyrene (WPS), a conjugated microporous polymer (CMP) was synthesised and activated into a sulphonic-group carrying resin (SCMP). The surface chemistry of the materials showed a decline in both the aromatic $-C-H$ and aliphatic $-CH_2-$ stretching vibrations confirming successful crosslinking. The synthesised polymers were thermally stable with decomposition temperatures above 300 °C, had surface heterogeneity, and BET surface areas of 752 and 510 m^2/g, respectively. A distribution of pores ranging from meso- to micro-pores was comparable to other CMPs. The materials had maximum adsorption capacities of 500 and 357 mg/g for Congo Red (CR) on CMP and SCMP, respectively. Converting waste polystyrene to an adsorbent is a cost effective way of handling waste and simultaneously providing material for wastewater remediation.

1. Introduction

Conjugated microporous polymers possess micro- and sometimes nano-porosity together with π-conjugation that confer both porosity- and conjugation-based properties. Their porosity makes them useful as adsorbents for both gases and liquids, and as gas storage materials for a variety of applications. Some of these applications include CO_2 capture and H_2 storage, and the π-conjugation confers electrical properties making them suitable for use in electrical energy storage, sensors, and photocatalysis (Dawson et al., 2012; Xu et al., 2013, 2014; Ratvijitvech et al., 2014; Ma et al., 2015). Conjugated microporous polymers enjoy the advantages of tunable pore structures, high surface area, chemical and thermal stability (Meng et al., 2013). A number of techniques, all of which employ virgin materials, have been used to synthesise conjugated microporous polymers. These include the Sonogashira-Hagihara coupling, Suzuki coupling, Yamamoto, Ullman reactions and the Fridel-Crafts reactions (Ahn et al., 2006; Schmidt et al., 2009; Deng et al., 2015; Vinodh et al., 2015; Bao et al., 2016). The characterisation of conjugated microporous polymers is generally limited by their poor solubility in common solvents. However, commonly used characterisation techniques include attenuated total reflectance fourier-transform infrared spectroscopy (ATR-FTIR), solid state NMR (ss-^{13}C NMR), Ultraviolet–visible diffuse reflectance spectroscopy (DRS-UV), thermo-analytical techniques, and porosimetry measurement techniques (Vinodh et al., 2015). Other useful techniques are positron annihilation lifetime spectroscopy (PALS) and ^{129}Xe NMR, that have been used to study PIM-1 and related polymers, for example (Emmler et al., 2010; Harms et al., 2012). A number of researchers have also used computer modeling techniques to predict the properties of conjugated microporous polymers (Abbott and Colina, 2014; Bonakala and Balasubramanian, 2016).

On the one hand, contamination of water by the toxic dyes from the dye manufacturing, textile, cosmetic, pulp and paper, and plastic industries is well documented (e.g., Abbas and Trari, 2015; Zare et al., 2015; Kalpana and Selvaraj, 2016; Lafi et al., 2016; Li et al., 2016; Yuan et al., 2016). Treatment of dye effluent is generally a challenge because the dyes are resistant to chemical and biological degradation (Ausavasukhi et al., 2015; Chaukura et al., 2016a; Kumari et al., 2016). Dyes thus pose an environmental and public health risk because they drastically reduce photosynthetic activity by aquatic plants and consequently cause environmental risks to biota and humans (Abbas and Trari, 2015; Ausavasukhi et al., 2015; Chan et al., 2016; Shayesteh et al., 2016). Congo Red

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(CR) [1-naphthalene sulphonic acid, 3,3′-(4,4′-biphenylenebis (azo)) bis (4-amino-) disodium salt] is widely used for the direct dyeing of cotton. Because of its complex aromatic structure and stability, CR is resistant to biodegradation. With fresh water sources dwindling due to climate change and other factors, the removal of dyes from water is therefore a priority, and a variety of technologies have been used including membrane technology, coagulation, photocatalysis, precipitation and adsorption (Abbas and Trari, 2015; Zare et al., 2015; Kalpana and Salvaraj, 2016; Kumari et al., 2016; Shayesteh et al., 2016). Of these approaches, adsorption is a cost-effective alternative because of ease of availability of sorbent feedstocks, simplicity of design, simple operation, low maintenance and high removal efficiency (Abbas and Trari, 2015; Ausavasukhi et al., 2015; Chaukura et al., 2016b; Shayesteh et al., 2016). At present, activated carbon is the most widely used adsorbent for dye removal, but this is limited by the high cost of the material, pore clogging, hygroscopicity, flammability and challenges associated with regeneration and disposal of spent adsorbents (Meng et al., 2013). It is therefore imperative for research to look for cheaper adsorbents that can efficiently remove dyes from water.

On the other hand, post-consumer waste polystyrene (WPS) is a non-biodegradable solid aesthetic pollutant whose low density facilitates its ease of spread by the wind (Hussain et al., 2012; Undri et al., 2014; Ruziwa et al., 2015; Chaukura et al., 2016c). Its disposal by incineration is costly, produces toxic chemicals like polyaromatic hydrocarbons (PAHs) and greenhouse gases that have a harmful impact on the environment and to humans, while disposal in landfills is limited by space and can result in leaching of toxins into the soil and potentially contaminate surface and groundwater (Hussain et al., 2012; Chaukura et al., 2016c). Research interest has recently focused on thermally depolymerising WPS into fuel and chemical feedstocks, and the re-use of WPS in various applications including construction materials, decor, and as adsorbents with modest removal capacities for heavy metals (Bekri Abbes et al., 2006; Hussain et al., 2012; Undri et al., 2014; Bartoli et al., 2015; Ruziwa et al., 2015). The development of sorbent materials from waste such as post consumer polystyrene makes it cost-effective approach. While some researchers have used virgin polystyrene precursor materials for the synthesis of conjugated microporous polymers (e.g. Davankov et al., 2000; Vinodh et al., 2015) and magnetic nanocomposites (Gu et al., 2016a, 2016b), we are not aware of the use of post-consumer waste polystyrene (WPS) in this regard. In any case, the applications of the conjugated microporous polymers has been mainly for gas sorption, energy storage, light harvesting, chemo- and bio-sensing, and catalysis, while applications in sorption of liquids is limited (Zhuang et al., 2013; Xu et al., 2014; Gu et al., 2015). Pristine WPS is not suitable to adsorb substances from aqueous solution because the surface is hydrophobic and lacks functional groups and porosity. In this work we hypothesise that WPS can be used as a precursor for the synthesis of porous and functionalized conjugated microporous polymers with dye removal properties comparable to materials derived from virgin polystyrene and related materials. The aim was to prepare a hypercrosslinked and a sulphonated conjugated microporous polymer from WPS and investigate their use in the removal of CR from aqueous solution.

2. Materials and methods

2.1. Synthesis of adsorbents

All reagents and solvents were purchased from Sigma-Aldrich, South Africa and used without any further purification. Distilled water was processed through a Milli-Q purification system, Millipore obtained from Microfiltration, Johannesburg South Africa. Discarded food trays made from polystyrene were collected from the university canteen at UNISA, Florida campus and washed with detergent, rinsed with distilled water then dried at room temperature over night. The dry trays were then cut into small pieces (about 1 cm^2) and a 10 g aliquot placed into a 500-mL two-neck round-bottom flask containing 100 mL of anhydrous ($\geq$99.8%) dichloromethane (DCM). To this was added 5 mL of 99% dimethoxymethane (DMM) and 0.50 mg of 99.99% $FeCl_3$ and refluxed for 8 h at 80 °C under constant agitation. The resulting precipitate was washed with methanol (100 mL), followed by a 1:1 acetone/water mixture with 5% HCl (200 mL). Thereafter the material was dried in an oven at 70 °C overnight before being ground to <500 μm then characterised and activated. This material was coded CMP. Activation of CMP into sulphonated CMP (SCMP) was performed following a method by Ruziwa et al. (2015). Specifically, 5 g of CMP was placed in a 250 mL round-bottomed flask and 100 mL of 98% H_2SO_4 added slowly. The mixture was brought to 70 °C and refluxed for 1 h. Thereafter, the synthesised polymer was washed with deionised water and dried at 70 °C overnight and ground to <500 μm consistency. The synthetic process is summarised in Scheme 1.

2.2. Characterisation of adsorbents

Determination of pH was performed on a 1:10 solid:water extract. The surface morphology of the synthesised CMPs was characterised with scanning electron microscope (SEM) (QuantaTM 250 FEG, Questar, USA) at 40 μm magnification after coating the surfaces of CMP and SCMP with a carbon film. Infrared spectra were recorded using a FTIR spectrometer (Thermofischer, Nicolet iS5, USA). A total of 4 scans were carried out for each sample in the range 4000 to 650 cm^{-1} with a resolution of 4 cm^{-1}. Both solid state and solution UV–Vis measurements were performed using a Lambda 650S, Perkin Elmer spectrophotometer. The porous structures of CMP and SCMP were characterised with N_2 sorption isotherms collected at 77 K using a physisorption analyser (TriStar 3000 V6.08 A, Micromeritics, Norcross, USA) after degassing for 3 h at 120 °C. Thermal stability of the materials was determined in the range 25–800 °C using TGA SDT Q600 analyser at a heating rate of 10 °C/min under a 20 mL/min flow of N_2 gas following the method by Shi et al. (2015). Zeta potential measurements were performed on an elecrokinetic analyser (SurPass, Anton Paar, Austria). Raman spectra were recorded using a Raman spectrometer (Witec 300 SMFC VIS-NIR, Germany) that uses a 532 nm He-Ar laser excitation source with a power of 0–90 mW.

2.3. Congo Red adsorption

Batch sorption experiments were performed using 20 mL of 60 mg/L initial concentration (C_i) of CR (save for the effect of initial CR concentration investigation) at 25 °C (save for the effect of solution temperature investigation). The sorbent loaded solution was stirred in 50 mL stoppered centrifuge bottles at 200 rpm using a thermostatic shaker (CNW, Thermostatic shaker, PSI-320) until equilibrium was reached. Thereafter, the samples were centrifuged at 2000 g and the supernatant analysed for CR at 498 nm on a UV/Vis spectrophotometer. The effect of contact time (30–180 min), pH (1.5–12), sorbent dosage (5–100 g/L), initial CR concentration (5–100 mg/L), and solution temperature (25–45 °C) were investigated for the sorption of CR on both sorbents. To assess any sorption by experimental vessels, blank runs without the sorbent were performed for each experimental condition. Triplicate runs were performed for each investigation and mean values reported. Required pH values were achieved using 0.1 M NaOH or HCl. For adsorbent mass, m in a total volume, V of solution, the amounts of