



# Structured emulsion-templated porous copolymer based on photopolymerization for carbon capture



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## ARTICLE INFO

### Keywords:

Porous polymer  
Photopolymerization  
Adsorption  
Absorption  
Carbon capture

## ABSTRACT

Porous hydrogel copolymers of acrylamide (AAM) and acrylic acid (AAC) were structured in the form of monoliths and granules. AAM-co-AAC porous copolymer monoliths were synthesized using high internal phase emulsion (HIPE) as template and photopolymerization. For granulation, photopolymerization was used for the fabrication of the AAM-co-AAC hydrogel, which was subsequently freeze-granulated. The structural analysis (FTIR and XRD) confirmed the successful synthesis of hydrogel copolymers. The CO<sub>2</sub> uptake capacity of structured AAM-co-AAC copolymers was evaluated through adsorption and absorption mechanisms by volumetric and gravimetric methods, respectively. The granules exhibited the CO<sub>2</sub> adsorption uptake of 0.8 mmol g<sup>-1</sup> at 25 kPa and 298 K. The CO<sub>2</sub> and N<sub>2</sub> adsorption data demonstrated that the hydrogel copolymers were selective for CO<sub>2</sub>. Furthermore, the granules were capable of capturing CO<sub>2</sub> in the presence of water. The results of absorption of CO<sub>2</sub> on water-swollen granules demonstrated that CO<sub>2</sub>-uptake capacity increases with increasing water content up to 1.8 mmol g<sup>-1</sup>.

## 1. Introduction

Porous polymers combine the properties of both porous structure and polymers for a variety of applications such as; separation and gas storage materials [1], filtration/separation membranes [2], scaffolds for controlled release of drugs [3], supports for cell scaffolds [4], low-dielectric constant materials [5], proton exchange membranes [6] and for many other applications. The ease of processing of porous polymers provides opportunities to structure these materials in form of beads, monoliths, laminates and thin films [7]. Furthermore, the diversity of synthesizing methods gives the possibility to functionalize pore surface [8] to demonstrate stimuli-responsive properties like changing the pore structure reversibly or swapping between the open and closed porosity [9,10]. These properties offer advantages in comparison to inorganic porous materials for their use as a membrane for selective CO<sub>2</sub> capture and separation [11].

Several technologies have been proposed to cut CO<sub>2</sub> emissions to atmosphere e.g. by using carbon-neutral energy sources, increasing the energy efficiency and capturing of CO<sub>2</sub> from point sources. The capture of CO<sub>2</sub> emissions from stationary point sources, fossil fuel power plant, has received much attention in recent years as it permits the use of fossil fuels for energy generation ensuring CO<sub>2</sub> elimination from the mixed gas byproduct. Up-and-coming CO<sub>2</sub> capture technologies are wet scrubbing with the physical and chemical absorbents, solid dry

scrubbing with sorbents, cryogenic separation, and separation utilizing CO<sub>2</sub>-selective membranes [12]. The CO<sub>2</sub> capturing technology is chosen depending on the number of variables such as byproduct gas temperature and pressure, desired capture efficiency, CO<sub>2</sub> partial pressure, concentrations of pollutants, process costs, and potential environmental impacts of the method. The simplest solvent for CO<sub>2</sub> absorption would be water scrubbing, however, a variety of solvents such as the alkanolamines, amino acid salts, ionic liquids and their blended aqueous solutions have been used for wet scrubbing of CO<sub>2</sub> [13–15]. The solid adsorbents for CO<sub>2</sub> sorption have been reviewed recently [16–19], and categorized into non-carbonaceous scaffolds (e.g., silica, zeolites and alkali metal), carbonaceous materials (e.g., activated carbons, graphene, metal-organic frameworks and covalent organic frameworks). Herin, the use of polymer based porous materials for CO<sub>2</sub> separation by sorption has been promising because these materials are tailorable, energy efficient and scalable [20].

The high internal phase emulsion (HIPE) as template (discontinuous phase) is used to synthesize porous polymeric membrane with pore sizes ranging from μm to nm [21]. These porous scaffolds including hydrophobic/hydrophilic polymers are synthesized through free radical polymerization within water-in-oil (W/O) emulsions for hydrophobic structures and oil-in-water (O/W) emulsions for hydrophilic structures. Polymerization of the continuous phase of a (W/O) HIPE is a versatile method for the preparation of highly porous polymers for filtration

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media [22], chromatographic columns [23], and scaffolds for tissue engineering and cell growth [24,25]. Nonetheless, there are fewer reports on the use of the inverse (O/W) polyHIPEs, where the aqueous phase containing monomers is used as a continuous phase, for the preparation of hydrophilic materials. Reports on the preparation of hydrophilic polyHIPEs include AAM, N-isopropyl acrylamide (Ni-PAAM), acrylic acid (AAC), 2-hydroxyethyl methacrylate (HEMA), and hydroxyethyl acrylate (HEA) monomers [21,26–28]. In contrast, other methods like super-critical carbon dioxide in water HIPEs and sedimentation polymerization have been utilized for the preparation of hydrophilic materials such as polyacrylamide polyHIPEs [26,29–31]. Despite a few exceptions (i.e. microfluidic porous particle)[32] preparation of porous polymeric membranes and scaffolds using photopolymerization technique is rare in the literature. Other methods are usually based on free radical polymerization and thermal initiation that are slower than UV initiated method. The formation of porosity in radical polymerization is based on phase separation and solvating power of the porogen and is strongly dependent on temperature. Thus, the temperature during the photopolymerization should not exceed 60 °C to avoid influencing the photopolymerization [33].

The present work describes the preparation of porous polymeric scaffolds using HIPEs. We propose photo-polymerization technique as a fast and simple method to design and structure porous polymeric scaffolds utilizing HIPEs. Towards this objective, AAM and AAC monomers, commonly used photosensitive polymers in photo-polymerization, have been used for the preparation of porous hydrogel copolymers to combine the properties of individual polymers into a single structure. The synthesized scaffolds were characterized through Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), surface area analysis and water uptake experiments. The CO<sub>2</sub> adsorption and absorption properties of dry and wet, respectively, hydrogel copolymers in the form of monolith and granules were reported.

## 2. Materials and methods

### 2.1. Material

The used materials were as; Acrylamide (AAM) monomer, Acrylic acid (AAC) monomer, N,N'-methylene bisacrylamide (MBA) and 2,2-Dimethoxy-2-phenylacetophenone from Sigma–Aldrich company. Paraffin oil ( $\rho = 0.827\text{--}0.890$ ) from Sigma–Aldrich and distilled water were used for the preparation of O/W HIPE. Toluene (Sigma–Aldrich), ethanol (Merck Co.), acetone (Merck Co.), and Span 80 (Sigma–Aldrich), were all used as received.

### 2.2. Methods

#### 2.2.1. Preparation of AAM-co-AAC monolith

AAM-co-AAC monoliths were prepared by an inverse polymerization, within oil-in-water (O/W) emulsion ratio of 1:4. AAM and AAC monomers were prepared in molar compositions of 90:10 (mol/mol) and dissolved in an equal weight of ethanol as the solvent. MBA (10% w/w monomer mixture) as crosslinker, 2,2-Dimethoxy-2-phenylacetophenone (1% w/w monomer mixture) as an initiator, Span 80 (20% v/v organic phase) as a surfactant and distilled water as porogen were added to the monomer mixture while stirring to completely dissolve the reagents. A white emulsion was formed upon adding paraffin oil drop by drop under stirring at 500 revolutions per minute (rpm). Then, the mixture assembly was transferred to a UV source preset at 365 nm wavelength and intensity of 17.5 mW cm<sup>-2</sup>. Photopolymerization occurred in 5 min where paraffin operated as a template for porosity and the obtained hydrogel copolymer was carefully removed. The chemical reaction mechanism was shown in Fig. 1. All synthesized samples were washed by soxhlet extraction in toluene for 24 h and followed by extraction in acetone for 24 h and dried in a freeze dryer. The procedure is

shown as a schematic in Fig. 1(path (a)).

#### 2.2.2. Preparation of AAM-co-AAC granules

AAM-co-AAC granules were prepared by photopolymerization and freeze granulation methods. AAM and AAC monomers were prepared in molar compositions of 90:10 (mol/mol) and dissolved in an equal weight of ethanol as the solvent. MBA (10% w/w based on monomer mixture) as crosslinker, 2,2-Dimethoxy-2-phenylacetophenone (1% w/w based on monomer mixture) as initiator were added to the monomer mixture under stirring to completely dissolve the reagents. Then, the mixture was transferred to a UV source preset at 365 nm wavelength and intensity of 17.5 mW cm<sup>-2</sup>. Where photopolymerization occurred in 5 min. Freeze granulation method involves spraying droplets of a liquid or suspension into liquid nitrogen container followed by freeze-drying of the instantly frozen droplets [34]. Here, distilled water was used as a solvent to swell AAM-AAC hydrogel copolymer and prepare a suspension. The AAM-co-AAC hydrogel suspension was sprayed into liquid nitrogen in a freeze-granulator (PowderPro Freeze granulator LS-2), which the drops were instantly frozen into granules. Subsequently, obtained granules were dried in a freeze dryer. The procedure is shown schematically in Fig. 1(path (b)).

#### 2.2.3. Characterization of AAM-co-AAC hydrogel copolymers

**2.2.3.1. FTIR analysis.** Synthesized AAM-co-AAC hydrogel copolymers were characterized by fourier transform infrared spectroscopy technique between 500 and 4000 cm<sup>-1</sup> utilizing Spectrum One, Perkin-Elmer (USA) equipment.

**2.2.3.2. XRD analysis.** The X-ray diffraction data of AAM-co-AAC hydrogel copolymers was recorded by a PANalytical Empyrean instrument equipped with a PIXcel3D detector using Cu-K $\alpha$  radiation at 40 KV and 45 mA settings. The data was analyzed using High Score Plus software (vers.3.0.1).

**2.2.3.3. Scanning electron microscopy (SEM).** Morphology and microstructural analysis of hydrogel copolymer granules and monoliths were carried out by scanning electron microscopy (JEOL JSM 6064LV, USA). The appropriate amount of the sample was mounted on a metal plate by Leit-C conductive carbon (Plano GmbH, Wetzlar, Germany) prior to insertion into the microscope.

**2.2.3.4. BET.** Nitrogen adsorption experiment was performed at 77 K on a Micrometrics Gemini V 2390 apparatus (Micromeritics, Norcross GA, USA). Prior to adsorption measurements, the samples were degassed at high vacuum ( $1 \times 10^{-4}$  Pa) at 353 K for 24 h. The Brunauer–Emmet–Teller (BET) surface area was calculated utilizing the nitrogen uptake of the sample in the relative pressure range of 0.01–0.30 p/p<sub>0</sub>.

**2.2.3.5. CO<sub>2</sub> adsorption measurements.** The CO<sub>2</sub> and N<sub>2</sub> adsorption measurement was performed using volumetric methods on a Micrometrics Gemini V 2390 apparatus (Micromeritics, Norcross GA, USA). All samples were degassed at high vacuum ( $1 \times 10^{-4}$  Pa) at 353 K for 24 h. The adsorption measurements were done at 298.15 K within a pressure range from 0 to 90 kPa. Isothermal conditions ( $\pm 0.1$  K) were maintained by a water bath where the temperature in the bath controlled by an external thermometer. Moreover, the cyclic performance of the samples was measured by recording the CO<sub>2</sub> uptake of the samples after regeneration under vacuum at 298 K. The well-known Langmuir isotherm model (i.e. as follow) was used to explain the adsorption behavior of CO<sub>2</sub> and N<sub>2</sub>:

$$q = \frac{q_m bP}{1 + bP} \quad (1)$$

where  $q$  is uptake,  $q_m$  is the maximum uptake,  $P$  is the equilibrium pressure and  $b$  is equation constant.

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