



CO₂ capture by ion exchange resins as amine functionalised adsorbents

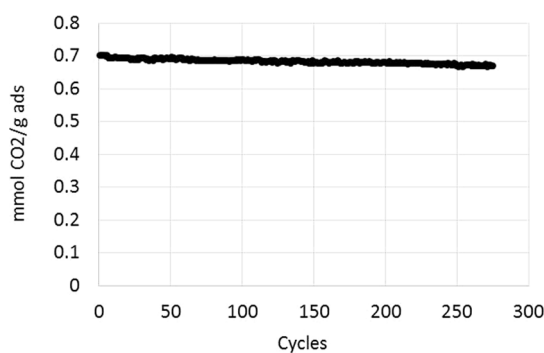


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GRAPHICAL ABSTRACT



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ABSTRACT

In this work, the performance of ion exchange resins as amine functionalised CO₂ adsorbents is evaluated. These resins are D201 and D202 of Jiangsu Suqing Water Treatment Engineering Group Co., Ltd, Purolite A109, A830 and Lewatit VPOC1065. A109 and VPOC1065 show higher CO₂ adsorption performance than D201, D202 and A830. VPOC1065 and A109 are functionalised with primary amines on a polymeric support of styrene cross-linked with divinylbenzene. Their capture capacity is examined at different temperatures, ranging from 25 to 80 °C, and different CO₂/N₂ ratios (0.02–0.98) in a dry gas mixture, using thermogravimetric analysis. VPOC1065 and A109 show a capacity of 1.75 and 1.12 mmol/g ads at 25 °C and 98% CO₂/N₂, respectively. Complete regeneration at 105 °C can be achieved for both resins and they exhibit fast adsorption and desorption kinetics. Cyclic adsorption-desorption tests are also performed and VPOC1065 shows excellent stability in 275 cycles. Hence, VPOC1065 and A109 ion exchange resins proved to be promising candidates for CO₂ adsorption.

1. Introduction

The main source of energy for the coming decades seems to be fossil fuels [1]. Fossil fuels emit CO₂ in the atmosphere, which contributes to the greenhouse effect and climate change. For sustainable use of fossil fuels, CO₂ emission management is of vital importance. Fossil fuel-fired power plants are one of the major sources of CO₂ emissions [2]. The separation of CO₂ from other gases has been clearly conducted for a few

decades in the natural gas industry as usually reservoirs contains some amounts of CO₂ [3]. Commercial CO₂ capture processes are based on using alkanolamine solvents such as monoethanolamine (MEA) but the main drawbacks of these liquid amine-based processes are their high regeneration energy, solvent degradation, equipment corrosion and scale up problems [4].

Porous solid adsorbents with low heat capacities represent an interesting alternative to amine aqueous systems for CO₂ capture, due to

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their higher gas phase mass diffusion into the porous support and elimination of corrosion of process equipment. However, CO₂ adsorption by porous solid adsorbents still needs more work, which is mainly focused on optimizing adsorption performance by developing appropriate materials [5,6]. Most widely used porous solid materials are silica, alumina, zeolite, carbon and more recently polymeric and MOF materials. The amine groups can be immobilised on porous support solids in favour of chemisorption that enhances capacity and selectivity in comparison with physisorption [7,8]. For adsorbents to be competitive with aqueous amine solutions, a stable capacity of about 3 mmol CO₂/g ads is desirable in flue gas conditions [9]. Many works have been done on CO₂ adsorption but more research is needed in order to develop solid adsorbents with optimum performance for CO₂ adsorption [6,9–11].

Impregnation techniques have been widely used to functionalise porous support materials. Although the impregnation technique increases adsorption capacity due to high level of amine loading but, possible amine leaching into the gas phase reduces cyclic adsorption-desorption stability [12–15]. To overcome amine leaching (amine evaporation) it is possible to immobilise the amine by covalent bonding with the porous solid support [16]. But the amine loading is limited to the functional groups in the support [10,17–21].

Porous polymeric materials have been used as porous solid support for functionalization with amines. Impregnation method was used in a number of works for amine functionalisation of polymethylmethacrylate (PMMA) as porous polymer support [22–26]. More works have been done with porous polymers with N functionality for CO₂ capture as support materials [27–34]. Chitsiga et al. [35] applied poly-succinimide (PSI) as support and covalent bonding using grafting technique with water-soluble amines to study CO₂ capture.

A class of polymeric materials that are generally used for water treatment are ion exchange resins (IERS). They are crosslinked polymers normally based on acrylic or styrene monomers. These polymers are functionalised with amines as anion exchanger in water treatment. For water treatment, they are mainly functionalised with quaternary amines to preserve exchange capacity in a wide range of pH. Other amines are used for some special purpose cases. The macroporous anion exchangers can be regarded as potential candidates for CO₂ capture as amine functionalised adsorbents. A few studies have been done on IERS using Lewatit VPOC1065 that is functionalized with primary amine. Alesi and kitchin [16] evaluated the CO₂ capture capacity of commercial Lewatit VPOC1065 anion exchange resins. They reported a CO₂ capture capacity of 2.5 mmol CO₂/g ads at 50 °C and dry gas conditions for 100% CO₂ using Cahn TG-131 thermogravimetric analyser (TGA). By exposing the resin to a dry gas mixture of 10% CO₂ in N₂, the adsorption capacity is about 1.55 mmol CO₂/g ads in a fixed bed reactor. Eighteen cycles of temperature swing regeneration were done with 10% CO₂ in N₂ gas mixture and adsorption temperature of 50 °C and desorption of 120 °C. They observed no apparent reduction in adsorption capacity. These resins shipped wet containing about 50% water. The resin was dried at 110 °C for 3 h in N₂ to remove moisture before performing adsorption experiments. Veneman et al. [36] also examined the Lewatit VPOC1065 materials for post combustion CO₂ capture. The highest CO₂ capture measured was 2.8 mmol CO₂/g ads at 30 °C, 70 kPa pressure in 80 vol% of CO₂ gas mixture, dry condition using

NETSZCH STA 449 F1 Jupiter thermal gravimetric analyser (TGA). By increasing the temperature, capture capacity decreased. They examined the H₂O uptake in humid gas conditions. Their results showed the CO₂ uptake is not affected by the co-adsorption of H₂O. The sample was heated up to 80 °C in N₂ to desorb any pre-adsorbed CO₂ and moisture. Hallenbeck et al. [37] investigated the stability of VPOC1065 in the presence of O₂ and SO₂. The degradation against O₂ was examined by 17 cycles of adsorption/desorption via a thermal swing between 50 and 127 °C and using a test gas of 12 vol% CO₂, 4% O₂, 84% N₂ in a fixed bed reactor. A stable cyclic adsorption-desorption capacity of about 1.27 mmol CO₂/g ads was reported. A test gas of 12.5 vol% CO₂, 4% O₂, 431 ppm SO₂, and balance N₂ was used to evaluate the stability against SO₂ over the same number of cycles. After 12 cycles the capture capacity linearly reduces to about 0.2 mmol CO₂/g ads (from the average of 1.27 mmol CO₂/g ads).

In this work a few available anion exchange resins are examined to evaluate existing commercial resins. These resins are developed for water treatment and therefore not necessarily optimised for CO₂ capture. Lewatit VPOC1065 and Purolite A109 are both functionalised with primary amines. Most ion exchange resins are functionalised with quaternary amines for water treatment. D201 and D202 of Jiangsu Suqing Water Treatment Engineering Group Co., Ltd and Purolite A830 are also evaluated for CO₂ adsorption using a dry gas mixture of CO₂ in N₂. D201 and D202 are functionalised with quaternary amine and A830 with complex amine based on the manufacturer data sheet. The study is focused on A109 and VPOC 1065. The resins were dried in a tube directly from wet under N₂ and 110 °C for 50 h to be sure that there is no moisture in the core of the beads. Another issue with these resins is their shrinkage in the absence of moisture [16]. Since our experiments are performed in dry conditions, 50 h of drying was used to be sure about structural stability and no extra shrinkage in the course of experiments particularly cyclic adsorption-desorption tests. CO₂ adsorption in a temperature range of 25–80 °C and CO₂/N₂ ratio of 0.02–0.98 is investigated. Different desorption temperatures under pure N₂ were studied to obtain complete desorption. Cyclic adsorption-desorption tests to study the stability and durability of the adsorbents are performed.

2. Methodology

2.1. Resin samples

Five different commercial macroporous ion exchange resins are evaluated in this work including D201 and D202 of Jiangsu Suqing Water Treatment Engineering Group Co. Ltd., Purolite A109 and A830 and Lewatit VPOC1065. A summary of manufacturer data is shown in Table 1.

For Lewatite VPOC1065 textural properties are reported by manufacturer as: BET surface area of 50 m²/g, pore volume of 0.27 cm³/g and pore size of 25 nm. For other samples manufacturer has not provided any textural data. The chemical formula of amine groups are not reported by manufacturers.

Table 1
Manufacturer data on the commercial ion exchange resins used in this work.

Ion exchange resins	Amine group	Ion exchange capacity	Particle size mm	Moisture	Support materials
VPOC 1065	Primary amine	2.2 eq/lit	0.315–1.25	65–70%	Polystyrene-divinylbenzene
A109	Primary amine	1 eq/lit	0.425–1	58–65%	Polystyrene-divinylbenzene
D201	Quaternary amine	0.95–1.2 mmol/ml (3.7 mmol/g)	0.315–1.25	50–60%	Polystyrene-divinylbenzene
D202	Quaternary amine	3.6 mmol/g	0.315–1.25	47–57%	Polystyrene-divinylbenzene
A830	Complex amine	2.75 eq/lit	0.3–1.2	50–56%	Polyacrylic-Divinylbenzene

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