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Effect of the presence of water-soluble amines on the carbon dioxide (CO_2) adsorption capacity of amine-grafted poly-succinimide (PSI) adsorbent during CO_2 capture

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Abstract

Global climate change is among the major challenges the world is facing today, and can be attributed to enhanced concentrations of Greenhouse Gases (GHG), such as carbon dioxide (CO_2), in the atmosphere. Therefore, there is an urgent need to mitigate CO_2 emissions, and carbon capture and storage (CCS) is amongst the possible options to reduce CO_2 emission. Against this background, this work investigated the synthesis and performance evaluation of a new material for CO_2 capture. In particular, the effect of the presence of water-soluble amines in the amine-grafted poly-succinimide (PSI) (referred to as Polyaspartamide (PAA) adsorbent), was investigated. Methyl Amine (MA) and Mono-Ethanol Amine (MEA) were employed as water-soluble amines and the effect of changes in their concentration on CO_2 adsorption capacity was investigated as well. Water-soluble amines were incorporated to allow water solubility of the adsorbent paving way for freeze-drying to improve the geometric structure (surface area, pore volume and pore size) of the adsorbent. The water-soluble amines were grafted to an already Ethylenediamine (EDA) grafted PSI (PSI-EDA), with the EDA added to improve the chemical surface of the adsorbent for CO_2 capture. The NMR analysis confirmed the presence of MA and MEA amine groups in the PAA, thereby indicating the presence of the grafted amines on the backbone polymer. An increase in adsorption capacity with an increase in MA and MEA concentrations in MA-PAA and MEA-PAA samples was observed. At low amine concentrations (20% amine and 80% EDA grafted), MEA-PAA was observed to exhibit higher adsorption capacity compared to the MA-PAA samples. At high amine (100% amine grafted) concentrations, MA-PAA samples displayed higher adsorption capacity. Three runs were performed on each sample and the results obtained were reproducible. The best adsorption capacity obtained was 44.2 g CO_2/kg Ads. However, the operating conditions during the CO_2 adsorption should be optimized for enhanced CO_2 adsorption capacity.

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Keywords: Climate change; Carbon dioxide capture; Amine-grafted polymer; Polysuccinimide; Polyaspartamide

1. Introduction

Global climate change is among the major challenges the world is facing today, and can be attributed to enhanced concentrations of Greenhouse Gases (GHG), such as carbon dioxide (CO_2), in the atmosphere. In sub-Saharan Africa, South Africa, whose economy predominantly depends on coal for energy production, is the largest emitter of CO_2, and is thirteenth globally [1-4]. Therefore, there is an urgent need to mitigate CO_2 emissions in South Africa, and carbon capture and storage (CCS) is amongst the possible options to address this. Amongst the promising CCS techniques in use are absorption and adsorption. Absorption is a mature technology with about 100% efficiency for CO_2 capture, but it is cost intensive due to large quantities of energy required for desorption and regeneration of the solvent, and the environmental unfriendliness of the spent solvent [2]. Alternatively, adsorption requires less energy compared to absorption and the materials employed may be environmentally more friendly. These advantages show that with adsorption lower operational costs may be achieved; its application in post-combustion capture in coal fired power plants may be carried out economically. However, new materials displaying large capacities for CO_2 capture are required to make adsorption competitive to absorption. Adsorption also has drawbacks which include slower kinetics and poor heat transfer in the packed beds [2]. Adsorption can be chemical or physical, with chemical adsorption involving the formation of chemical bonds between the adsorbate and the adsorbent [5]. Physical adsorption is caused by intermolecular Van der Waals' forces as well as electrostatic forces occurring between the adsorbent and the adsorbate molecules [6-8]. Adsorbents are characterized by their properties which include surface area, pore size, pore volume and functional groups within the adsorbent which influence the nature of adsorption [9]. These properties influence the adsorption isotherms which govern the adsorbent-adsorbate equilibrium. More so, for industrial application, the adsorbent-adsorbate equilibrium affects the capacity, selectivity, regenerability, kinetics, compatibility and cost of the adsorbent [8, 9]. Several adsorbents have been developed and these include carbon molecular sieves, zeolites, activated carbons and more recently amine-grafted polymers and metal organic frameworks (MOFs) [10]. Amine-grafted polymers have become very popular and are a promising type of adsorbent. The potential stems from the currently widely applied method (absorption) which makes use of amine solvents such as Polyethylenenimine (PEI) to capture CO_2 [11]. An amine-grafted polymer consists of a backbone, which is the polymer, and an amine, which is attached to the polymer to act as the anchoring site onto which the CO_2 attaches. The CO_2 attaches to the anchoring site by formation of a weak intermediate carbamate (-COO-) as it reacts with the amine [12]. Amine groups are incorporated due to their high affinity for CO_2 and they also stabilize the CO_2 adsorption process as they form stable intermediates. Furthermore, the adsorption process is reversible; the adsorbent can be recovered by use of different types of desorption such as Temperature Swing Adsorption (TSA), Pressure Swing Adsorption (PSA), Electric Swing Adsorption (ESA) or Vacuum Swing Adsorption (VSA) [11].

An adsorbent should have a large surface area and a large enough pore size to enable the adsorbate (CO_2) to adsorb to it [5, 7]. These properties can be improved by use of a process known as freeze-drying. Freeze-drying is used extensively in the food and drug industry to improve properties such as pore volume, pore size and surface area. Freeze-drying is a process where mass and heat are both transferred simultaneously from a material resulting in an improved physical and chemical composition as well as microstructure [13, 14]. The material to be freeze-dried may contain water already or may be dissolved in water and is frozen by use of liquid N_2 [13, 14]. Thereafter, the frozen water is sublimated and removed, leaving the material with an improved microstructure displaying higher porosity. A higher porosity implies that the pore size as well as the surface area of the material has increased [13, 14]. Furthermore, freeze-drying is beneficial in that it can be applied to materials which are temperature sensitive because no heat is added, it prevents shrinkage of materials, and it reduces the possibility of material deterioration reactions due to almost complete dehydration of the material [13, 14]. Freeze-dried materials have a spongy and highly porous structure which is desirable in adsorption processes [14].

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Against this background, the current work investigated the synthesis and performance evaluation of a new material for CO_2 capture. In particular, the effect of the presence of water-soluble amines in the amine-grafted poly-succinimide (PSI), herewith referred to as Polyaspartamide (PAA) adsorbent, was investigated. Methyl Amine (MA) and Mono-Ethanol Amine (MEA) were employed as water-soluble amines and the effects of the change in their concentration on CO_2 adsorption capacity was investigated as well. The water-soluble amines were grafted to an already Ethylenediamine (EDA) grafted PSI (PSI-EDA), with the EDA added to improve the chemical surface of the adsorbent for CO_2 capture to enhance the CO_2 adsorption capacity. The solubilizing group was added to enhance the water solubility of the adsorbent to enable the adsorbent to dissolve in water paving way for freeze-drying to improve the geometric structure of the solid adsorbent. The dissolution of the adsorbent in water could enhance the CO_2 desorption process.

2. Experimental

2.1. Materials

Phosphoric acid, D. L. Aspartic acid, Dicyclohexylcarbodiimide (DCC), Ethylenediamine (EDA), Sodium hydroxide and solvents such as N, N-Dimethylformamide (DMF > 99 %), Acetone and Ethyl Ether, were all obtained from Sigma-Aldrich, South Africa. The liquid N_2, gaseous N_2, carbon dioxide and air were of analytical grade obtained from Afrox, South Africa.
A rota-vapor R 114 was used during the synthesis of the PSI, the backbone polymer. All glassware and magnetic stirrers were obtained from the laboratory. A thermo-gravimetric analyzer (TGA), TA STD Q600, was used to determine the thermal stability of the synthesized adsorbent as well as for determination of the CO_2 adsorption capacity of the adsorbent.

2.2. Synthesis of PSI and the water-soluble amine-grafted PSI

PSI was synthesized from a poly-condensation reaction of aspartic acid in a phosphoric acid medium, as described by Ngoy [12] and Kumar [15]. The procedure depicted in Figure 1 was followed during the synthesis of PSI. D.L. aspartic acid was homogenized with phosphoric acid in a mass ratio of 2:1 in a 2 L volumetric flask. In each synthesized batch of PSI, 25 g of aspartic acid was used with 12.5 g of phosphoric acid due to available glassware capacity. The flask was then heated in an oil bath to 250 ^oC while rotating on a rota-vapor to ensure vacuum conditions as well as uniform heating of the reaction. A vacuum pump was used to create the necessary vacuum conditions. Liquid N_2 was used to protect the pump from damage by the chemicals that should be pulled out of the reactor during the vacuum process. The expansion was monitored and controlled by use of N_2 gas. At the end of the expansion, the reaction temperature was reduced to 190 ^oC and maintained at this temperature for 2 hrs. The product obtained was washed with distilled water and filtered off until the pH was between 6 and 7. Indicator paper was used to determine the pH of the reaction product. The washed product was further placed in an oven at 45 ^oC for 72 hrs to dry it. The resultant mass was recorded and the product was dissolved in N, N Dimethylformamide (DMF) in preparation for coupling and grafting.

1g of oven product was dissolved in 4.04 ml of DMF. The brownish solution obtained from the dissolved oven product was stirred for 12 hrs. in a flask. The flask was then cooled using an ice bath and stirred for another hour, DCC was added then, as a coupling agent for the lengthening of the polymer chain in order to multiply the available sites for adsorption, at a ratio of 1 g of DCC to 8.57 g. The resulting solution in the flask was stirred for 4 hrs resting in an ice bath, thereafter it was left to warm to room temperature for 12 hrs. A clear solution was produced from the brownish solution by use of a centrifuge. The clear solution was then precipitated by use of distilled water. This was achieved by stirring distilled water in a 4 L beaker by use of a magnetic stirrer; thereafter the centrifuged solution was added. Following the precipitation, the precipitate was filtered and dried at 45 ^{o}C in an oven for 48 hours to give a brittle solid, namely PSI. The synthesized PSI was grafted with two combinations of amines at a variable ratio in order to cover the backbone completely. Table 1 shows the amount of amine used, amine concentration, as well as amount of PSI used in the synthesis of the water-soluble amine-grafted PSI (PAA). In Table 1, adsorbent samples 1-5 make use of MA-EDA amine combination and adsorbent sample 6-10 make use of MEA-EDA combination. Within each of the two combinations of amines, the amount of PSI was kept constant, while the amine combination concentration was varied.

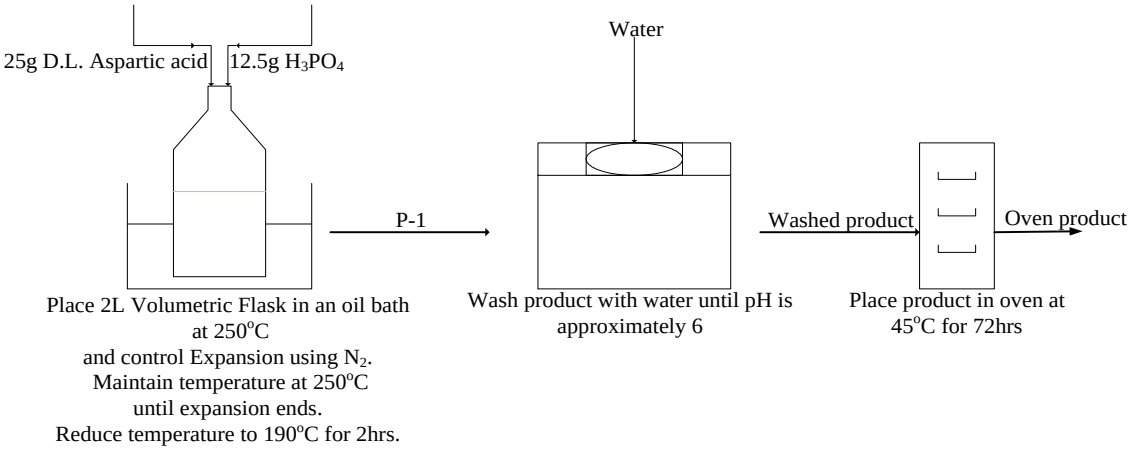

Fig. 1. Schematic showing the experimental procedure for the synthesis of PSI.

Table 1. Materials used in the synthesis of the PAA.

Sample	PSI amount (moles)	MA amount (moles)	MA fraction (%)	MEA amount (moles)	MEA fraction (%)	EDA amount (moles)	EDA fraction (%)
1	0.0305	0.0305	100	-	-	0	0
2	0.0305	0.0244	80	-	-	0.0061	20
3	0.0305	0.0183	60	-	-	0.0122	40
4	0.0305	0.0122	40	-	-	0.0183	60
5	0.0305	0.0061	20	-	-	0.0244	80
6	0.0305	-	-	0.0305	100	0	0
7	0.0305	-	-	0.0244	80	0.0061	20
8	0.0305	-	-	0.0183	60	0.0122	40
9	0.0305	-	-	0.0122	40	0.0183	60
10	0.0305			0.0061	20	0.0244	80

The PSI was dissolved in DMF (to prepare it for grafting) (3 g was dissolved in 15 ml), and was added to methyl-amine also dissolved in DMF in the same ratio. The resulting solution was flushed with N_2 gas and stirred for 24 hours at room temperature. With stirring, this solution was then added drop-wise to EDA dissolved in DMF, in the same ratio as PSI, and cooled in an ice bath. The solution was flushed with N_2 gas and stirred for 20 hours in the ice bath, followed by 5 hours at room temperature. Concentration of the solution on the rota-evaporator at 60 ^oC followed, to half the volume. Precipitation of the concentrated solution with a mixture of diethyl ether and hexane in a ratio of 2 to 1 followed. The precipitate was then washed with hot toluene followed by hot acetone, and then the precipitate was dissolved in distilled water. The solution was freeze-dried to obtain the water-soluble PAA. The amount of MA and EDA was varied and this procedure was repeated with the MEA-EDA combination, making use of the amounts shown in Table 1.

2.3. Characterization of the synthesized samples

Nuclear Magnetic Resonance (NMR) analysis, Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), N_2 physisorption (by BET analysis) and thermo-gravimetric analyses were performed to characterize the synthesized adsorbent. Thermal stability of the PAA was evaluated using 8 mg of the adsorbent in TGA. Each sample was heated to 900 ^oC in air and the temperature was increased in a step-wise ramp fashion from 25 ^oC to 700 ^oC with a ramp of 5 ^oC/min.

2.4. Evaluation of CO_2 adsorption performance of amine-grafted PSI (PAA)

The evaluation of the adsorption capacity of the synthesized PAA was done using a TGA. About 8 mg of each sample was used and the sample was then heated at a ramp rate of 5 ^oC/min to 110 ^oC, while N_2 gas was passed through the sample. The system was equilibrated at 110 ^oC for 30 min in the N_2 environment. This was done to drive off impurities such as water vapor from the sample. Thereafter, the temperature was dropped to 40 ^oC and

equilibrated at this value while simultaneously passing CO_2 gas (about 100 % purity) through at a flowrate of 60 ml/min. This was carried out for 3 hours at atmospheric pressure and thereafter the process was stopped. 100 % CO_2 was used to test for the adsorption performance because the material is novel and it is necessary to evaluate its performance in 100% CO_2 stream before using diluted gas stream and introducing some impurities as well.

3. Experimental

3.1. Characterization of PSI and amine-grated PSI (PAA)

NMR analysis was performed on the PSI product to confirm if the synthesis was qualitatively successful. The analysis was done in dimethyl sulfoxide (DMSO) solvent and Figure 2 shows the NMR spectra obtained. The peaks of importance are that of CH and CH_2 (starred in Figure 2), signaling the presence of two types of protons, the first in the shift range 3.5 – 2.9 ppm and the second in the range 5.8 – 4.8 ppm. There were, however, impurities that were picked up during the NMR analysis. These impurities included: dimethyl formamide (DMF), which was the solvent used during the synthesis of the PSI; water and morpholine which are common proton NMR impurities; and DMSO, the solvent used in the NMR analysis. The FTIR analysis of the sample depicted in Figure 3 shows the presence of all the functional groups (C-N, C=O and C-H) in PSI, thereby confirming the successful synthesis of the PSI. The C=O and C-H functional groups occur within the wavenumber ranges of 1650-1740 cm^{-1} and 3100-3200 cm^{-1} respectively. The functional group C-N, which occurs within the wavenumber range of 1430-1530 cm^{-1}, was shown to be present in PSI, and confirms the presence of the amide group which acts as the cleavage bond for biodegradability [12]. The FTIR analysis performed on the synthesized PSI closely resembles what was obtained in literature [12], again confirming the successful synthesis of the compound PSI. From the thermal stability analysis shown in Figure 4, PSI is safely stable up to a temperature of 400 ^oC, which is consistent with literature, hence again confirming the successful synthesis of PSI in this study [14, 16].

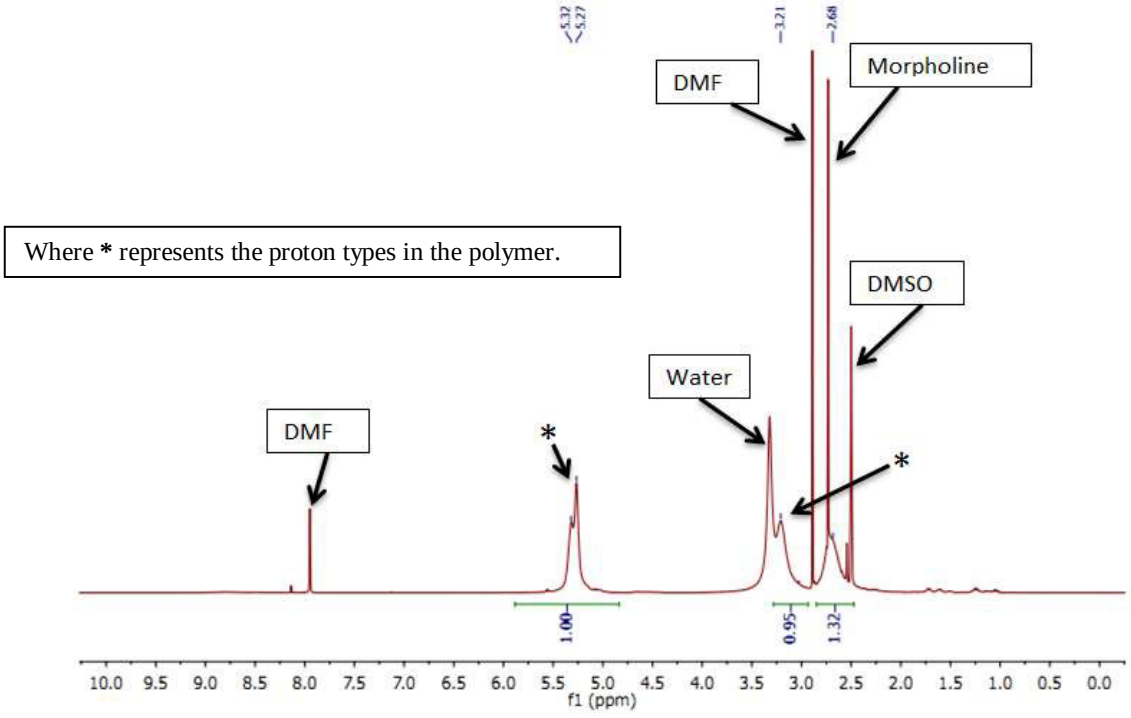

Fig. 2. NMR analysis of PSI confirming the expected structure qualitatively.

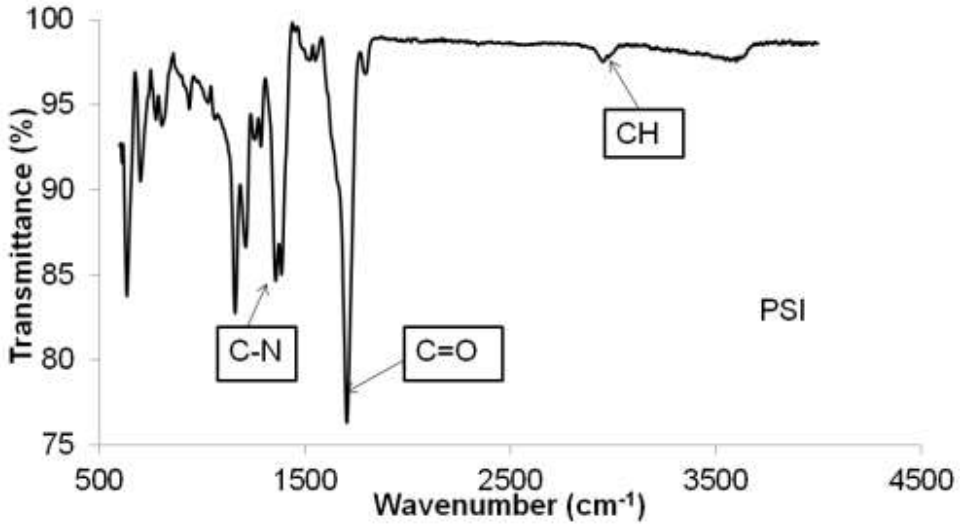

Fig. 3. FTIR analysis showing relevant peaks in the chemical structure of PSI.

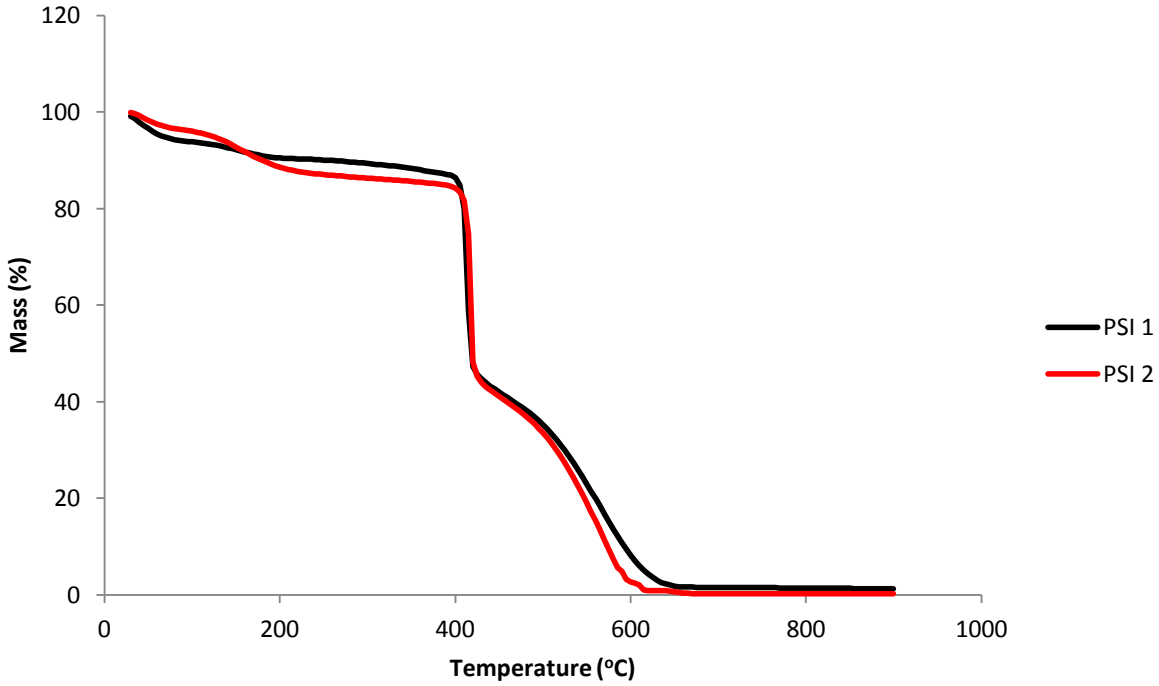

Fig. 4. Thermal stability analysis of the synthesized PSI showing variation of mass with temperature, comparing PSI 1 adapted from the study by [12], and PSI 2 – the sample from this study.

Figure 5 shows the reaction scheme of the synthesis of the amine-grafted PSI, being the PAA. The first reaction is

that of PSI with the water-soluble component; in this work MA and MEA were used, making the R-groups **-CH_3** and **–OH** for MA and MEA, respectively. The second phase of the reaction is that of grafting a second amine, a diamine, to the water-soluble amine-grafted PSI. In this work, ethylene diamine (EDA) was used as the second amine. The R-group in the EDA structure is **-CH_2CH_2-**.

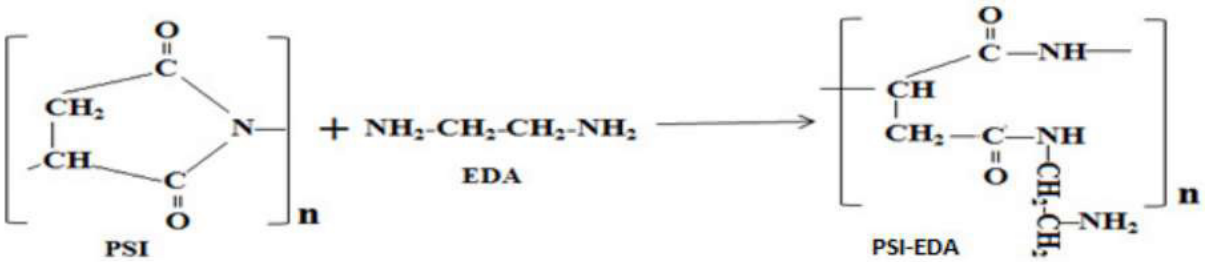

Fig. 5. Reaction scheme showing the formation of Polyaspartamide (PAA) which is an amine-grafted PSI [12].

NMR analysis was performed on the amine-grafted PSI (PAA) to confirm if the grafting was successful. The analysis was done in DMSO solvent, Figure 6 shows the proton NMR spectra obtained. The peaks of importance are those starred, confirming the presence of different proton types present in the amine-grafted PSI. Similar impurities to the PSI spectra were identified and are shown in Figure 6. Amine-grafted PSI samples with the highest MA and MEA concentrations and the lowest MA and MEA concentrations were selected for FTIR analysis. This was done with the assumption that the other concentrations would fall within this range of analysis. Figure 7 shows the FTIR analysis of PSI-MA-EDA, 100 % MA (Sample 1) and 20 % MA (Sample 5). Figure 8 shows the FTIR analysis of PSI-MEA-EDA, 100 % MEA (Sample 6) and 20 % MEA (Sample 10). Both figures show that the amines were successfully grafted onto the PSI. The expected functional groups were obtained from the FTIR peaks, -NH_2 between 3300 cm^{-1} and 3500 cm^{-1}, N-H between 3100 cm^{-1} and 3200 cm^{-1}, C=O between 1650 cm^{-1} and 1740 cm^{-1} and C-N between 1430 cm^{-1} and 1530 cm^{-1}. The –NH_2 group shows the presence of a primary amine in the synthesized adsorbent, which in contact with CO_2 has a potential of forming carbamate, a reversible bond.. The C=O, N-H and the C-N functional groups are part of the amide bond, which provides for biodegradability of the adsorbent by forming a bio-fission bond at which the molecule breaks. The presence of these functional groups confirms that the synthesized adsorbent is biodegradable [12].

Thermal stability of the synthesized adsorbent was evaluated using a TGA. The amine-grafted PSI samples showed a thermal stability of up to 210 ^oC, a 48 % reduction in thermal stability when compared with that of the original PSI sample (See Figures 9 and 10). This can be attributed to the fact that during the grafting of the amines, the chemical ring in the structure of PSI is opened as the amines are grafted onto it. The thermal stability of the PAA obtained in this study is consistent to that in literature [12].

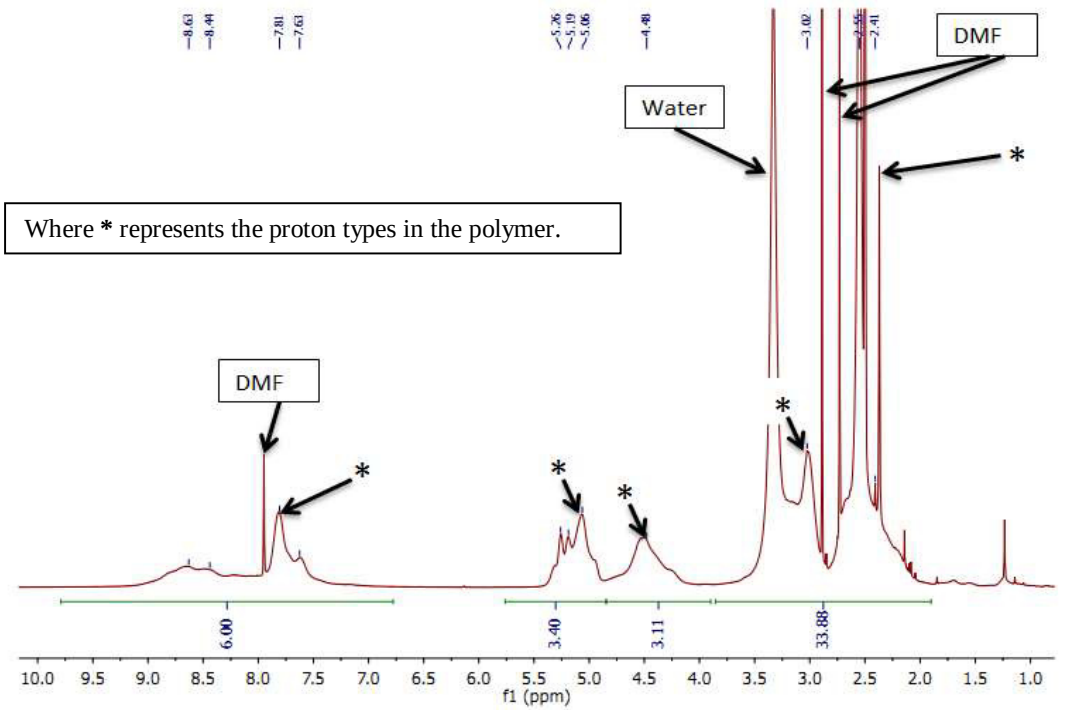

Fig. 6. NMR analysis showing relevant peaks in the chemical structure of PSI-MA-EDA.

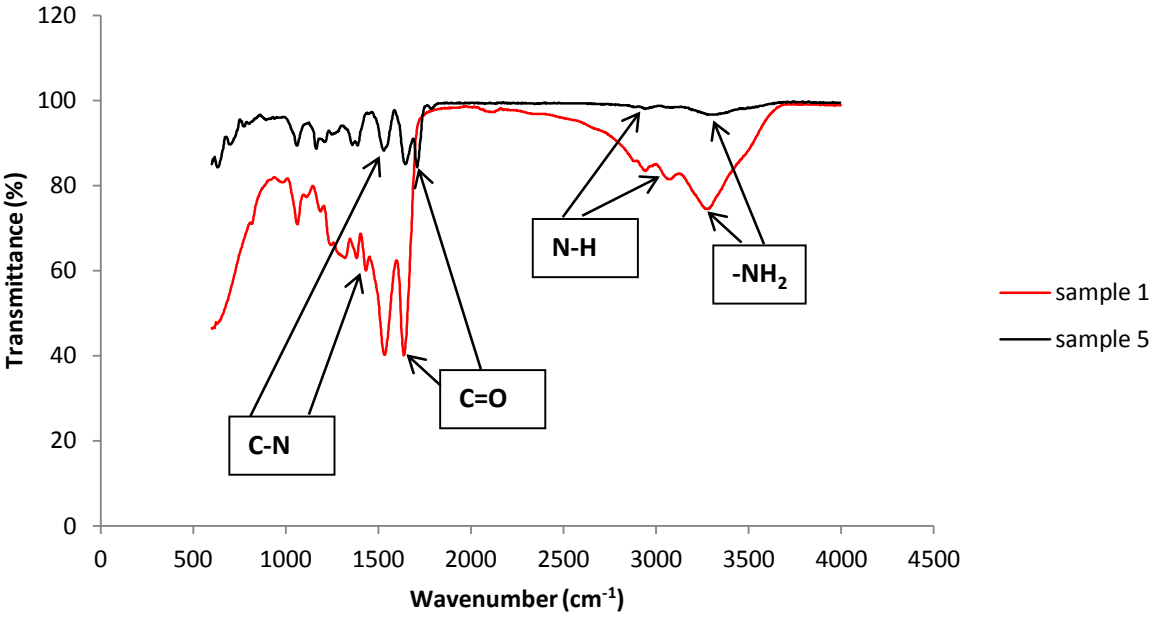

Fig. 7. FTIR analysis showing relevant peaks in the chemical structure of PSI-MA-EDA.

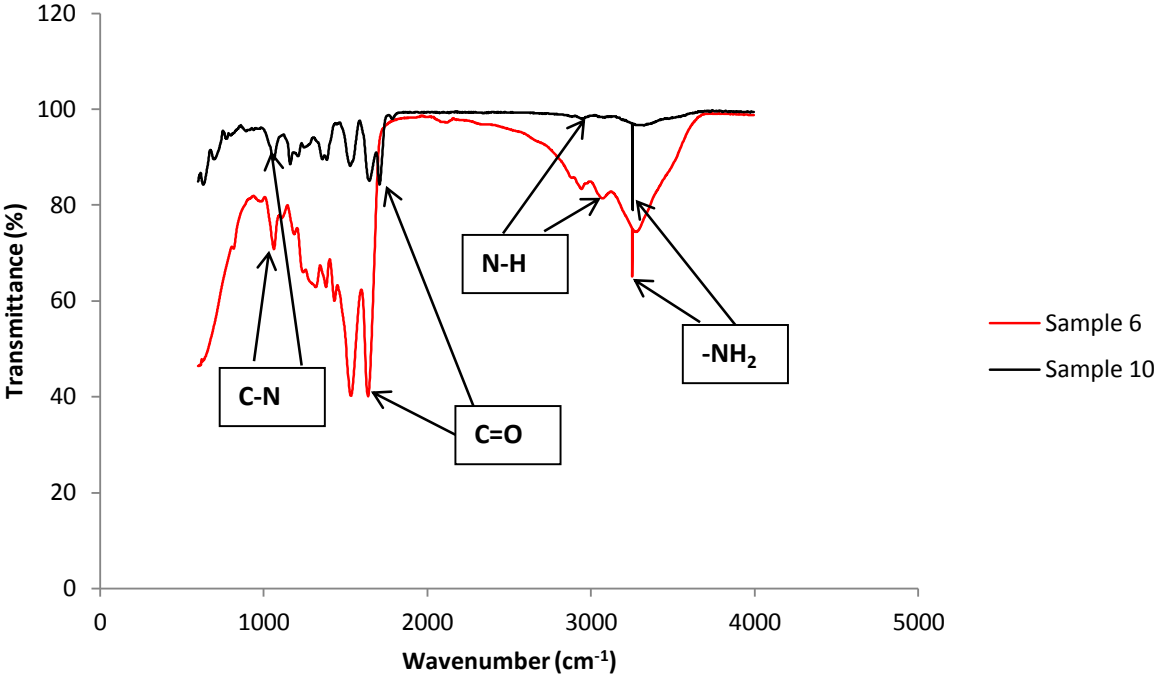

Fig. 8. FTIR analysis showing relevant peaks in the chemical structure of PSI-MEA-EDA.

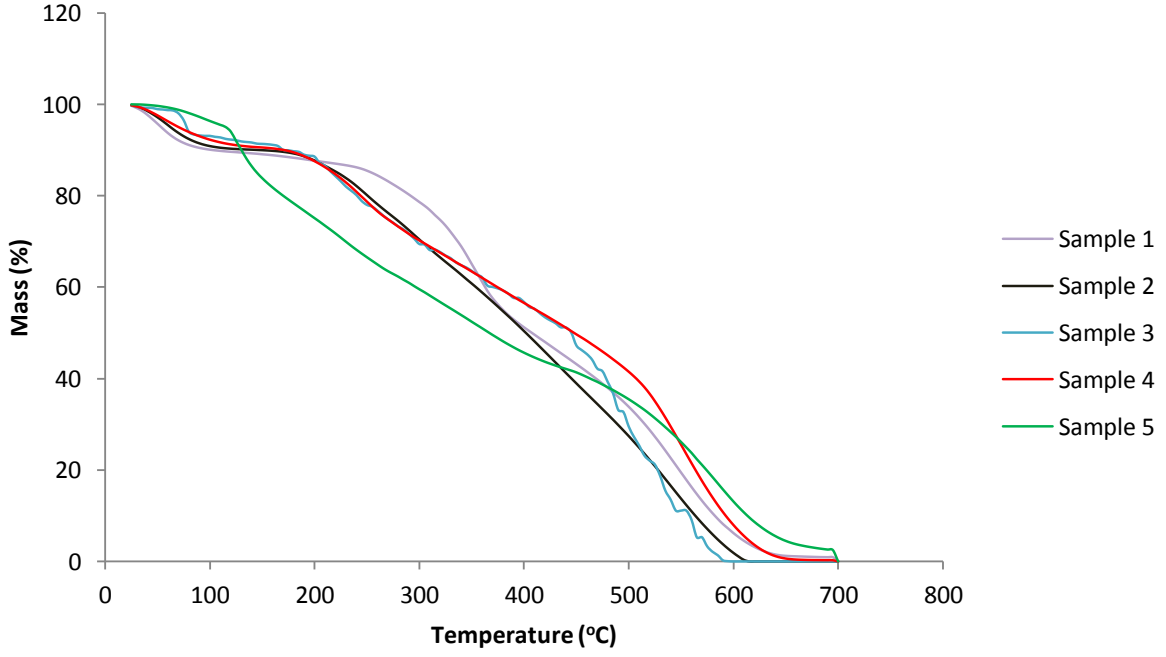

Fig. 9. Thermal stability analysis of PSI-MA-EDA samples showing variation of mass loss with temperature.

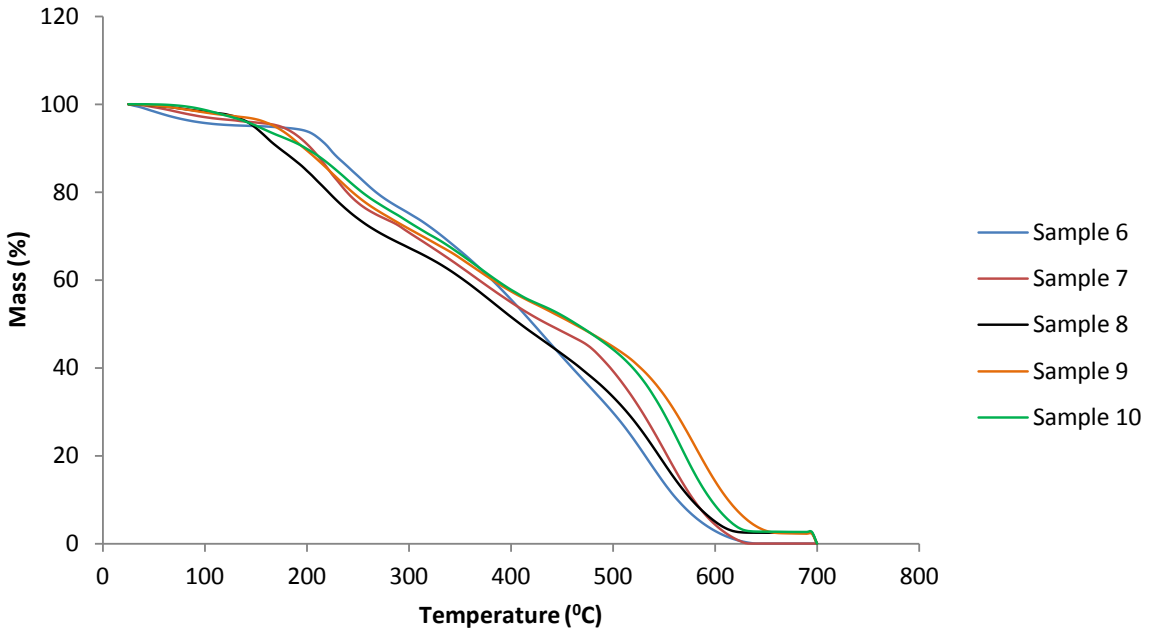

Fig. 10. Thermal stability analysis of PSI-MEA-EDA samples showing variation of mass loss with temperature.

BET analysis was carried out on all the synthesized amine-grafted PSI (PAA) samples to determine their pore size, pore volume and BET surface area (Table 2). In literature, PAA is shown to have a pore size of 20.63 nm, a pore volume of 0.01 cm^3/g and a surface area of 1.93 m^2/g [24]. Sample 1 to sample 10 in Table 2 show similar values for the same properties with small variations. The PAA from the report of Ngoy et al. [12] was obtained via a different drying method which did not involve freeze-drying. In this study, freeze-drying was used to prepare the adsorbent and the expectation was that the pore size, pore volume and surface area would significantly be improved. The pore size and the BET surface area of the synthesized PAA (samples 1 and 6) increased by approximately 50 %, while their pore volume remained unchanged in comparison to amine-grafted PSI (PAA) from [12].

Table 2. BET analysis of the synthesized samples, Samples 1-10.

Sample	Pore size (nm)	Pore volume (cm^3/g)	Surface area (m^2/g)
1 (100 % MA)	30.97479	0.018444	2.9446
2 (80 % MA)	26.78457	0.015319	2.6874
3 (60 % MA)	25.35419	0.011457	2.5847
4 (40 % MA)	23.54712	0.010149	2.1843
5 (20 % MA)	21.58498	0.010038	1.9546
6 (100 % MEA)	28.72746	0.015650	2.9667
7 (80 % MEA)	24.65874	0.014678	2.8247
8 (60 % MEA)	22.47981	0.012549	1.7436
9(40 % MEA)	22.68954	0.011247	1.5289
10 (20 % MEA)	20.45832	0.011134	1.4786

SEM images of the synthesized amine-grafted PSI (PAA) samples are depicted in Figure 11. Amine-grafted PSI

(PAA) samples with the highest MA and MEA concentrations and the lowest MA and MEA concentrations were selected for SEM analysis; samples 1 and 5 were thus selected for PSI-MA-EDA, and samples 6 and 10 were selected for PSI-MEA-EDA. The SEM images were taken at magnification of 2000 X. It was observed that as the concentrations of MA and MEA increased to 100 % onto the PSI, there was an increase in the 'thinness' of the adsorbent. This is observed by comparing the images for sample 5 and sample 1, as well as that of sample 6 and sample 10, which show how the structure of the amine-grafted PSI (PAA) changes as the amine concentration is varied. This 'thinness' also corresponds to an increase in surface area as the BET analysis shows so in Table 2. Samples 1 and 6 have the highest surface area. Samples with a combination of MA-EDA and MEA-EDA had granular structures and the SEM imaging shows the spheres in the sample representative of the granular structure.

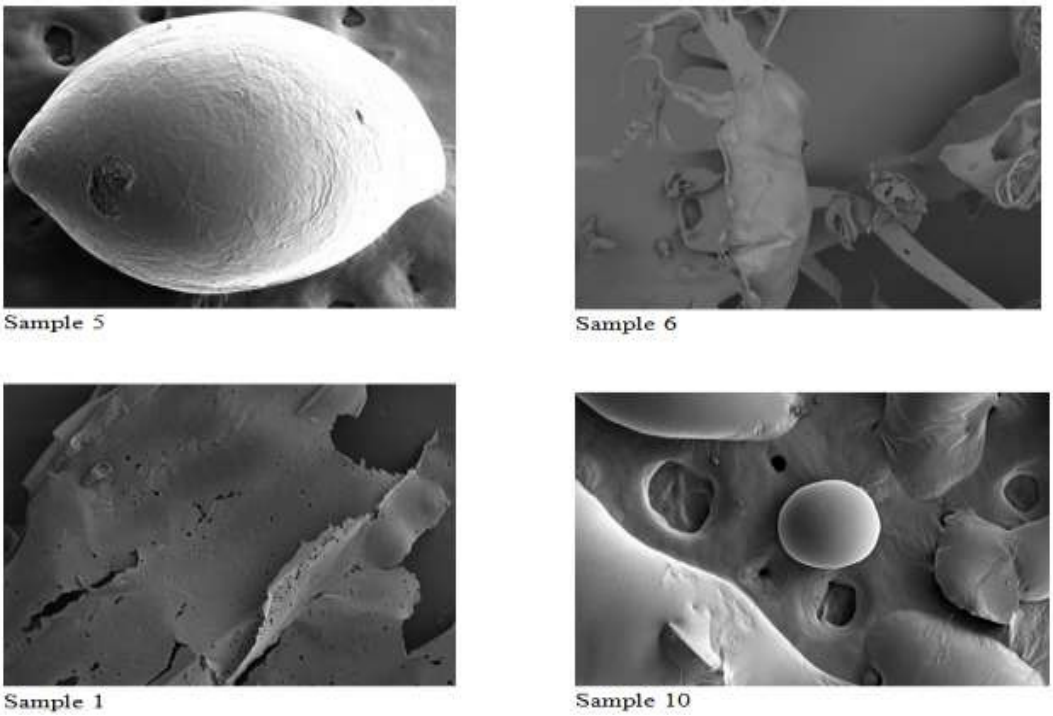

Fig. 11. SEM imaging of PSI-MA, PSI-MEA, PSI-MA-EDA (20 % & 100 % respectively), and PSI-MEA-EDA (20 % & 100 % respectively) to a magnification of 2000 X.

3.2. CO_2 adsorption performance of the amine-grafted PSI (PAA)

The CO_2 adsorption capacity of the adsorbent was determined in a TGA using pure CO_2 gas prescribed and ordered. Figures 12 and 13 depict the maximum adsorption kinetics of the samples. The CO_2 adsorption kinetics show that CO_2 adsorption capacity increased as the MA and MEA proportions were increased in the material (see Table 3). The operating conditions that were used in the TGA are: Temperature of 40 ^oC, Pressure of 1.1 bar and a flowrate of 60 ml/min.

Table 3. Adsorption capacities of synthesized samples.

Sample	Adsorption capacity (g CO_2/kg Ads)
1 (100 % MA)	44
2 (80 % MA)	12
3 (60 % MA)	7.0
4 (40 % MA)	11
5 (20 % MA)	5.0
6 (100 % MEA)	41
7 (80 % MEA)	18
8 (60 % MEA)	16
9(40 % MEA)	9.0
10 (20 % MEA)	9.5

A similar trend was observed for samples 10 through to 6 (see Table 3), with sample 6 giving the highest adsorption capacity of 41.5 g CO_2/kg Ads for the PSI-MEA-EDA samples. The observed trend shows that as the water-soluble component was increased in the adsorbent, the CO_2 adsorption capacity of the adsorbent improved. This may be attributed to the process of grafting two amines onto one polymer; the grafting may not have been achieved completely, resulting in a lower number of CO_2 anchoring sites available on the adsorbent for CO_2 capture. This may be due to the possibility of some of the amines (MA, MEA and EDA) to cross-link [12]. Cross-linking occurs when polymers are chained together due to ionic or covalent bonds [12]. In this particular adsorbent synthesis it results in no amine-grafting occurring due to the loss of reaction sites between the polymer and the amines as a result of cross-linking between the amines. Consequently, the number of CO_2 anchoring sites will be reduced. Samples 1 and 6 had only one amine each, the water-soluble component (MA and MEA) grafted onto them, as a result the grafting was successful and the adsorption capacity, which is higher than the remaining synthesized samples, is evident. The highest CO_2 adsorption capacity obtained in this study was 44 g CO_2/kg Ads which is comparable to what was found by [12], 47.1 g CO_2/kg Ads.

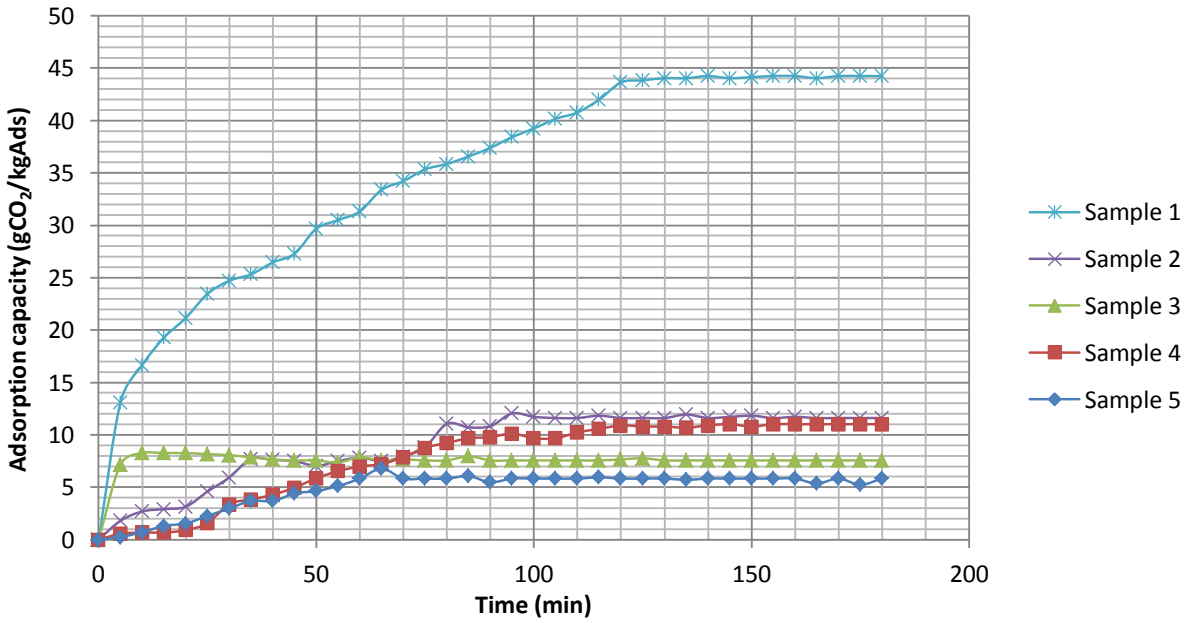

Fig. 12. PSI-MA-EDA adsorption capacity obtained from test runs in the TGA.

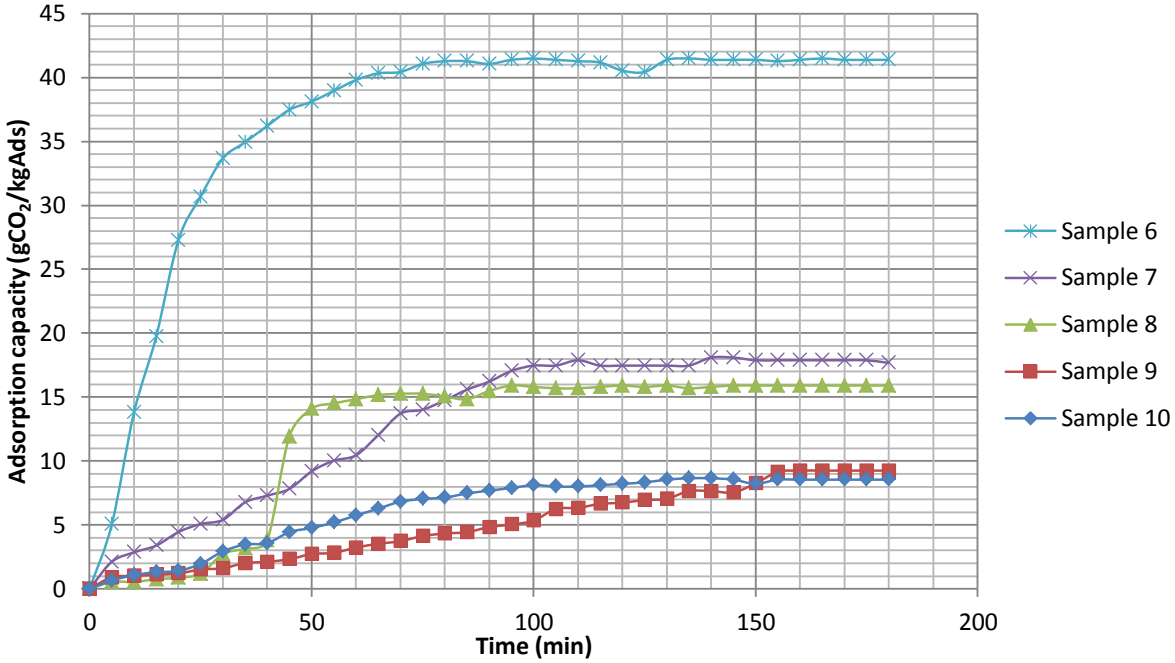

Fig. 13. PSI-MEA-EDA adsorption capacity obtained from tests run in the TGA.

In literature, several other adsorbents have been tested for CO_2 adsorption, such as zeolites, amine-rich nano-silicates, carbon-based adsorbents, metal organic frameworks, alkali-metal-based materials, amongst several others. Zeolites currently display high CO_2 adsorption capacities of 98 g CO_2/ kg Ads [10]. Carbon-based adsorbents perform even better than zeolites, with a reported adsorption capacity of 374 g CO_2/ kg Ads. However, the adsorption process conditions utilized to obtain these capacities are high pressures, as high as 10 bar [10]. This implies that higher process costs will be incurred in terms of operation to create such pressure values and capital to construct equipment to handle such pressures. The amine-grafted PSI synthesized in this work captures CO_2 at approximately atmospheric conditions which make it an attractive option for further consideration as a suitable CO_2 adsorbent. The kinetics of the adsorption process presented in Figures 12 and 13 are quite slow. This has been attributed to the positioning of the sample inside the TGA where the adsorption experiments were conducted. The gas flows over the pan in which the adsorbent is contained hence limiting contact between the adsorbent and the adsorbate. Contact between the adsorbate and the adsorbent is poor and thus impacts on the kinetics and possibly the capacity. There is therefore Polyethyleneimine infused and functionalized Torlon-silica hollow fiber sorbents have also been investigated and they have been reported to display adsorption capacities of approximately 431.2 g / kg Ads depending on the whether the Torlon is functionalized or not [31]. As the name, Polyethyleneimine infused and functionalized Torlon-silica hollow fiber sorbents, suggests, they are a different type of amine functionalized adsorbent. Compared to amine-grafted PSI sorbents presented in this paper, functionalized Torlon-silica hollow fiber sorbents are better adsorbents in terms of capacity but however the kinetics of the adsorption process are not reported hence they are of a concern.

4. Conclusion

In this work, a water-soluble amine-grafted PSI adsorbent was synthesized. The NMR analysis confirmed the incorporation of MA and MEA amine groups in the PAA, thereby indicating the presence of the grafted amines on the backbone polymer. TGA analysis showed that the synthesized adsorbent is thermally stable up to 250 ^{o}C. SEM analysis showed images characterized with an increase in ‘flakiness’ and pores as the MA and MEA concentrations were increased displaying a change in the geometric structure of the adsorbent. The BET analysis showed that the surface area, pore volume and pore size did not improve significantly as compared to amine-grafted PSI from

literature. An increase in adsorption capacity with an increase in MA and MEA concentrations in MA-PAA and MEA-PAA samples, respectively, was observed. At low amine concentrations (20 % amine and 80 % EDA grafted), MEA-PAA was observed to exhibit higher adsorption capacity compared to MA-PAA samples. At high amine (100% amine grafted) concentrations, MA-PAA samples displayed higher adsorption capacity. Three runs were performed on each sample and the results obtained were reproducible. The best adsorption capacity obtained was 44.2 g CO_2/kg Ads. However, the operating conditions during CO_2 adsorption should be optimized to enhance the CO_2 adsorption capacity. The kinetics reported in the experiments conducted using the TGA are of concern and this has been attributed to the poor contact between the adsorbate and the adsorbent due to the configuration inside the TGA. A packed bed reactor should be developed where the adsorbate flows through the adsorbent to improve adsorption kinetics and possibly capacity. Work on the packed bed is underway and results from the tests will be published as soon as they are available.

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