Preparation and long term stability studies of carbon dioxide adsorbents based on hyperbranched polymers

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Abstract: The article reports preparation and characterization of CO_2 adsorbents based on hyperbranched polyamines and polyglycerols. Hyperbranched polyglycerol containing primary amine groups (A-HBPG) and polyethyleneimine (PEI) showed to be effective in CO_2 capture from the ambient air. Adsorbents based on those polymers were stable for at least 17 adsorption/desorption cycles provided the desorption was performed in oxygen free atmosphere. Amine containing hyperbranched polymers are promising materials for CO_2 capture.

Keywords: hyperbranched polymer, carbon dioxide capture, polyglycerol, polyglycidol, amine.

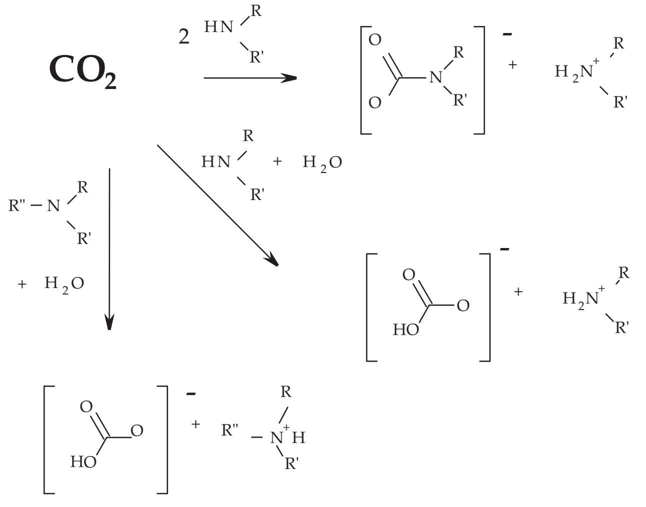
Otrzymywanie adsorbentów ditlenku węgla na bazie polimerów silnie rozgałęzionych oraz badania ich długoterminowej stabilności

Streszczenie: Scharakteryzowano adsorbenty CO_2 otrzymane na bazie polietylenoiminy (PEI) lub hiperrozgałęzionego poliglicerolu zawierającego grupy aminowe (A-HBPG) osadzone na różnych podłożach. Wykazano, że A-HBPG i PEI skutecznie wychwytują CO_2 z otaczającego powietrza. Badane adsorbenty wykazywały stabilność przez co najmniej 17 cykli adsorpcji/desorpcji CO_2, pod warunkiem, że desorpcję prowadzono w atmosferze beztlenowej. Stwierdzono, że hiperrozgałęzione polimery zawierające grupy aminowe są obiecującymi materiałami przeznaczonymi do wychwytywania CO_2.

Słowa kluczowe: polimer silnie rozgałęziony, wychwyt ditlenku węgla, poliglicerol, poliglicydol, amina.

Carbon dioxide (CO_2) is an important greenhouse gas, which is released through natural processes such as respiration and volcanic eruptions, as well as human activities such as deforestation and burning fossil fuels. CO_2 concentration in the air is at its highest level in the last 650 thousand years. The CO_2 levels measured at Mauna Loa Observatory, Hawaii, in recent 14 years raised by 34 ppm reaching level of 412 ppm [1]. There is an undeniable correlation between the observed global temperature rise, warming and acidification of oceans, shrinking of ice sheets, sea level rise and extreme weather events with enhanced atmospheric CO_2 concentrations. The resulting climate catastrophe owing to the surplus of CO_2 in the atmosphere is an immediate threat to our security and prosperity [2]. Therefore, a considerable effort has been focused to develop a range of chemical and physical methods for efficient CO_2 capture and sequestration [2–4].

Currently, the large-scale separation of CO_2 by the liquid phase amine-based absorption process is in commercial operation. This “wet-scrubbing” CO_2 capture utilizes alkanolamines, such as monoethanolamine, as the solvent [5]. During the absorption process, amine molecules in aqueous solution react with CO_2 to form water soluble compounds [6].



Scheme A. Reaction schemes for the chemical absorption of CO_2 by amines in presence or without presence of moisture

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As shown in Scheme A, two moles of secondary (or primary) amine species react with 1 mol of CO_2 under dry conditions to form carbamates. The reaction stoichiometry changes to 1 : 1 in the presence of moisture. In this case a bicarbonate is formed. Water is crucial for tertiary amines in the CO_2 capture process, in which 1 mol of amine species reacts with 1 mol of CO_2 to form bicarbonate as the final product. Amine-based systems can efficiently remove CO_2 from the flue gas of conventional power plants. However, they suffer a number of drawbacks, such as a volatility, a large amount of energy required for absorbent regeneration, equipment corrosion and their degradation in the presence of oxygen.

Several review articles dealing with CO_2 capture, specifically over the general solid adsorbents [7], nanoporous materials [8], MOFs [9], ionic liquids [10] and chemisorbents [11] have appeared in the literature. However, the amine-functionalization has been the universal concept applied to just about all different classes of materials [12].

The preparation of effective CO_2 adsorbents is still a challenge. They should be stable over many adsorption–desorption cycles [13]. The number of studies dealing with the stability of CO_2 adsorbents, particularly amine-containing polymers is still limited.

Recently we reported the synthesis of amine-containing HBPGs (hyperbranched polyglycerols) – polymeric analogues of ethanolamine and their characterization considering the capability of CO_2 adsorption from the ambient air.

In this work we investigated the stability of CO_2 adsorbents based on two polymeric materials (PEI and A-HBPG) and various supports. The first part of this study comprised preparation of CO_2 adsorbents based on metal coils, glass spheres and fumed silica and a model polymer – polyethyleneimine. The second part concerns the long term stability study of amine-containing HBPG and the selected CO_2 adsorbent support (fumed silica).

EXPERIMENTAL PART

Materials

All the reagents were purchased from Sigma-Aldrich (Poznań, Poland) and used as received. Solvents were purchased from POCh (Gliwice, Poland) or Chempur (Piekary Śląskie, Poland) and used as received except of tetrahydrofuran that was used immediately after distillation over potassium benzophenone ketyle (distillation to the reaction flask over argon). Prismatic coils made from stainless steel wire were obtained from Padew.pl (Poland), glass spheres made of neutral glass were obtained from labo24.pl (Poland), fumed silica (7 nm) was purchased from Sigma-Aldrich (Poznań, Poland). Two types of CO_2 adsorbing polymers were used in this studies: polyethyleneimine of the molar mass of 25 000 g/mol was purchased from Sigma-Aldrich (Poznań, Poland). Hyperbranched polyglycerol containing amine groups (A-HBPG) of molar mass 1000 g/mol was synthesized according to an improved two step one-pot procedure reported previously by us [14].

Synthesis of A-HBPG

Step 1

In a 1000 cm^3 three-neck flask equipped with a magnetic stirrer, a thermometer, a nitrogen inlet and a distillation condenser, 24 g (179 mmol) of trimethylolpropane (TMP) followed by 2.33 g (59.6 mmol) of potassium (metal chunks) were placed. Potassium was added in 4 portions in the flow of argon. After each addition the flask was immediately evacuated and the mixture stirred under vacuum at 80 °C until potassium completely reacted. Subsequently, the temperature was raised to 105 °C. The solution of 94.1 g (1.27 mol) of glycidol (96%) and 98.1 g (483 mmol) of glycidyl phthalimide [14] in 240 cm^3 of dry THF was then introduced with the rate of 6 cm^3/h by an infusion pump (Ascor Ap22). The solvent and any unreacted monomers were removed under vacuum (0.01 mmHg for 2 hours) leaving 220 g (99.9%) of the copolymer as pale yellow viscous oil.

Step 2

The distillation condenser was changed to reflux condenser and 500 cm^3 of ethanol added to the reaction flask. The mixture was heated at reflux to complete dissolution of the polymer. Then, 30.3 g (29.2 cm^3, 614 mmol) of hydrazine hydrate 65% aqueous solution was added and the resulting mixture stirred at reflux for 20 h until homogenous suspension was obtained. It was cooled down to room temperature. Hydrochloric acid was then added dropwise to a stable acidic pH. Obtained mixture was heated at reflux for an additional 60 min. The resulting slurry was transferred to a one neck 2000 cm^3 round bottom flask and evaporated almost to dryness under reduced pressure. The residue was diluted with 500 cm^3 of water. The precipitate of phthalhydrazide was filtered off. The clear filtrate was made alkaline (pH = 10) by addition of Na_2CO_3. The solvent was removed using a rotary evaporator. The residue containing the polymer was purified by multiple precipitation from methanol/ethanol mixture to remove any inorganic salts; 146.7 g (94%) of a light yellow viscous oil was obtained.

Analytical data of the products matched those published previously [14]. Elemental analysis showed content of 4.205 ± 0.015 wt % of nitrogen in the polymer sample which is in good agreement with the theoretical value (4.408%). The difference may be a result of loss of some low molecular weight oligoglycerols due to the procedure of multiple steps of washing and re-precipitation.

The synthesis of amine containing hyperbranched polyglycerols can be also performed using safer (without the use of potassium) and efficient method based on cyclic carbonate monomers [15].

Preparation of adsorbents

Sorbents based on prismatic metal coils

30 g of prismatic metal coils and 1 g of PEI were placed in a 100 cm^3 round bottom flask. 50 cm^3 of methanol was added. The contents of the flask were stirred until complete dissolution of the polymer. The solvent was removed by heating at 50 °C under vacuum on a rotary evaporator followed by vacuum treatment overnight (< 1 mm Hg). 0.7 g of PEI was coated on the coils. The surface area of the adsorbent was estimated to be 410 cm^2 (19.8 cm^2/g).

Sorbents based on glass spheres

80 g of neutral glass spheres of 2 mm diameter and 1 g of PEI were placed in a 200 cm^3 round bottom flask. 50 cm^3 of methanol was added. The contents of the flask were stirred until complete dissolution of the polymer. The solvent was removed by heating at 50 °C under vacuum on a rotary evaporator followed by vacuum treatment overnight (< 1 mm Hg). 0.637 g of PEI was coated on the surface of the spheres. The surface area of the adsorbent was estimated to be 960 cm^2 (11.9 cm^2/g).

Sorbents based on fumed silica

3 g of a polymer was dissolved in 50 cm^3 of methanol, then 3 g of fumed silica (7 nm) was suspended in 50 cm^3 of methanol. The solution of polymer was slowly added to the silica suspension to ensure a good dispersion of the polymer on the support. The suspension was then mixed for an additional hour. After that, the solvent was removed from the mixture by heating at 50 °C under vacuum on a rotary evaporator followed by vacuum treatment overnight (< 1 mm Hg). The supported amine sorbents were obtained as white to pale yellow solids. The grains of the sorbent of the size of 0.25 mm and smaller were removed on sieves. The specific surface area for the final PEI sorbent was approx. 24 m^2/g, while the value for A-HBPG 46 m^2/g.

Methods of testing

– FT-IR spectra were recorded on a Nicolet iS5 Mid Infrared FT-IR Spectrometer equipped with iD7 ATR Optical Base.

– ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian VXR 400 MHz or Bruker AVANCE 500 MHz spectrometers using tetramethylsilane as an internal standard and deuterated solvents ($CDCl_3$, DMSO-d_6).

– The average molecular weight of A-HBPG polymer was determined based on ^{1}H NMR spectra. The integral of the trimethylolpropane (TMP) core molecule CH_3 group was used as a reference.

– Carbon dioxide concentration was measured using HORIBA APCA-370 air pollution monitor.

– Elemental analysis was performed with Elementar Vario EL III CHNS analyzer. Nitrogen physisorption measurements using ASAP 2020 (Micromeritics Instrument Co.) were used to determine textural properties of the prepared materials.

– The specific surface area (S_{BET}) was determined by the multipoint Brunauer-Emmett-Teller (BET) method.

– CO_2 adsorption data were collected using a flow system. 3.0 g of an adsorbent was placed in a glass tube between two cotton plugs. The inner diameter of the tube was 8 mm. The heights of the adsorbent beds were about 7 ± 1 cm. The adsorbent tube was attached to vacuum (0.03 mm Hg) and placed in a heater at 85 °C for 3 hours. The mass of the adsorbent after this treatment was measured. The mass loss due to CO_2 and water desorption, depending on the adsorbent, was generally below 9%. The measurements were performed at 25 °C. The adsorbent containing tube was charged with an ambient air of average CO_2 concentration of 420 ppm and 35–90% relative humidity flowing through a thermostated (25 °C) copper tube coil. For the adsorption measurements a Horiba APCA-370 CO_2 analyzer equipped with an IR detector specifically intended for CO_2 measurements was used. The samples were analyzed with the 700 cm^3/min flow rate with the concentration range 0–2000 ppm. Almost immediately after starting the air flow onto the adsorbent, the CO_2 concentration in the outlet gas fell down (in some cases to 0 ppm), signaling CO_2 adsorption from the air. The CO_2 concentration was recorded as a function of time. After saturation of the adsorbent (12–72 h), when the CO_2 concentration reached the inlet value, the gas flow was stopped.

– Desorption was performed by heating the fumed silica based adsorbent containing tube up to 85 °C and then passing a flow of air (700 cm^3/min) through it. The outlet gas was analyzed on a Horiba APCA-370 CO_2 analyzer. The CO_2 concentration was recorded as a function of time. After starting the air flow onto the saturated adsorbent, the concentration of CO_2 increased. At 85 °C it spiked up and then slowly decreased until reaching the inlet CO_2 concentration (420 ppm). In selected experiments the adsorbent was regenerated by heating the tube under vacuum.

The experiments using metal coils and glass spheres were performed using the steel tube of 20 mm inner diameter and 250 mm length instead of a glass tube.

RESULTS AND DISCUSSION

The aim of this work was to develop and investigate the long term stability of the amine-containing A-HBPG based CO_2 sorbents. These studies had been preceded by the elaboration of procedures of preparation of CO_2 sorbents based on various supports and checking the influence of the type of support on the stability of the amine containing polymer.

For this purpose a measuring system was built consisting of a Horiba APCA-370 CO_2 analyzer, thermostat,

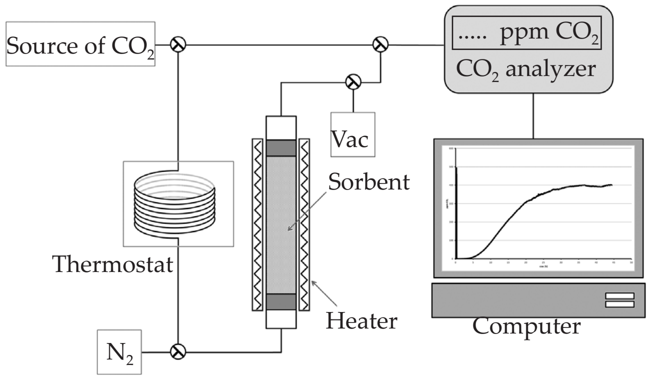


Fig. 1. The setup used for testing of CO_2 adsorption

tubular heater shown in Fig. 1. The set-up included nitrogen inlet and vacuum outlet allowing application of a variety of ways of sorbent regeneration. The source of CO_2 was the ambient air.

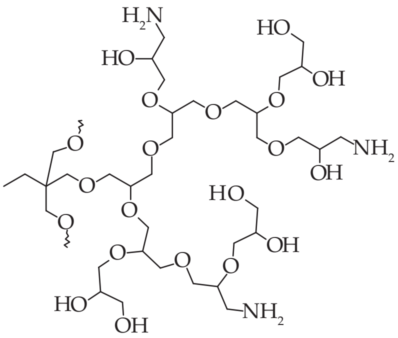
Our preliminary studies on fumed silica adsorbents showed that the physical appearance and a grain size of the sorbent has significant influence on the gas flow capability and the registered values of CO_2 concentration. In case of the sorbents made of fine and very fine powders and mixtures containing fine powder fraction the high flow resistance was observed. Because the gas flow was forced by the pomp placed at the outlet of the CO_2 analyzer, it resulted in generation of lowered pressure behind the adsorption bed and within the IR detector. The observed CO_2 levels were frequently lowered by 100 ppm or more.

Therefore, we struggled for finding a new testing device that would allow easy flow of the measured gas. Two testing environments were considered: one based on metal elements or glass spheres, second based on fumed silica.

The first choice were metal coils (stainless steel) or glass spheres placed in a metal tube. The expected advantage of such system, except to low flow resistance, was high thermal conductivity of the sorbent or metal body allowing fast desorption of adsorbed carbon dioxide. The expected inconvenience of such solution was possible oxidation of the sorbent.

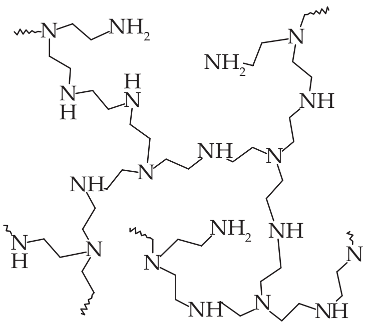
The second possibility was the proper preparation of fumed silica based sorbents of low flow resistance and optimization of the measurement conditions.

Two groups of polymers were investigated in these studies: a commercial polyethyleneimine and newly developed polymeric analogue of ethanolamine hyperbranched polyglycerol containing amine groups (A-HBPG). The structures of the polymers are represented by Formulas (I) and (II).



A-HBPG

Formula (I)



PEI

Formula (II)

PEI based sorbents

The first experiments were performed using PEI polymer and all metal setup using steel coils as a support for the polymer. Figure 2 shows the adsorption and desorption curves.

The amounts of CO_2 measured in the adsorption and desorption processes (Table 1) were at a comparable level. Steel supported polyethyleneimine adsorbed significant amounts of carbon dioxide. 0.7 g of PEI was capable of capturing all of the CO_2 from the passed air for approx. 1 hour. However, such behavior was observed only for

Table 1. Amounts of adsorbed and desorbed CO_2 for PEI deposited on steel coils

Adsorption/ desorption cycle	Adsorption			Desorption		
	mg CO_2	mg CO_2/g of PEI	mg CO_2/g of adsorbent	mg CO_2	mg CO_2/g of PEI	mg CO_2/g of adsorbent
I	81.1	115.9	2.64	50.7	72.4	1.70
II	10.7	15.3	0.35	12.7	18.1	0.41
III	2.5	3.6	0.08	6.5	9.3	0.21

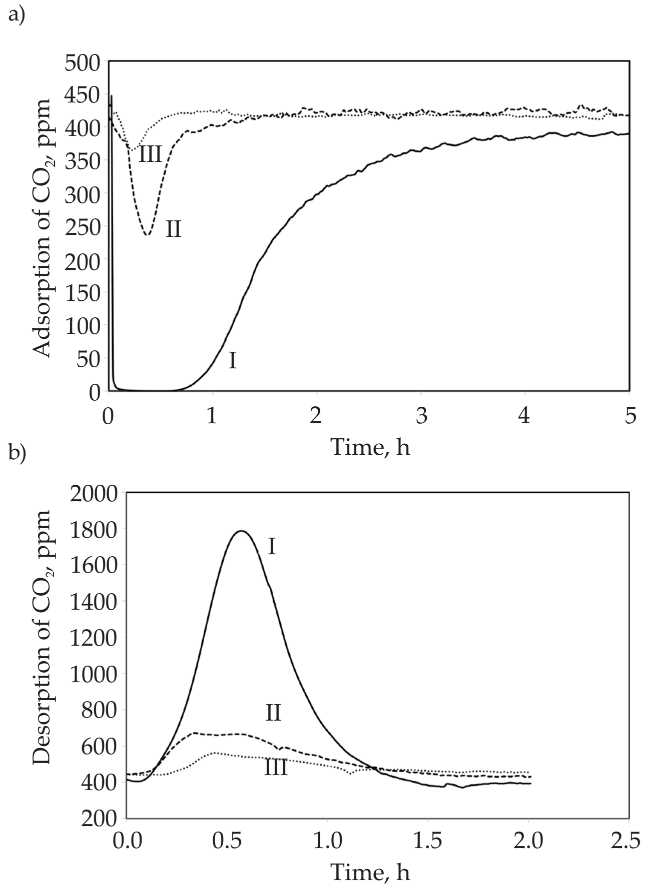


Fig. 2. Carbon dioxide: a) adsorption, b) desorption curves obtained for PEI polymer covered steel coils; I, II, III – numbers of adsorption/desorption cycles

the first run of the sorption process. Heating the adsorbent at 85 °C for 2 h to desorb CO_2 in the presence of air and steel support caused rapid polymer degradation. In the second pass, the amount of adsorbed carbon dioxide (Table 1) dropped drastically to about 10% of the initial value. In the third run only insignificant amount of CO_2 was adsorbed.

The changes in the adsorption properties were accompanied by strong color change and changes in the FT-IR spectra of the polymer, *e.g.* formation of the additional carbonyl absorption band at 1730 cm^{-1} (Fig. 3).

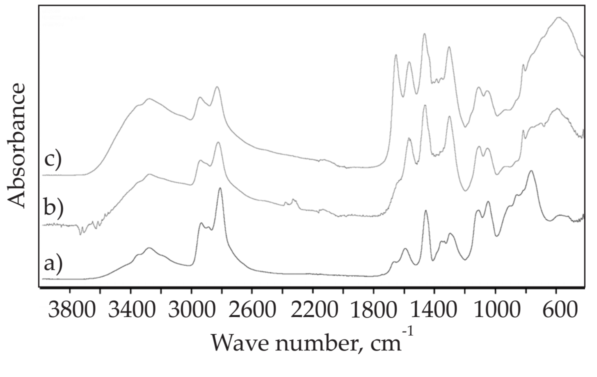


Fig. 3. FT-IR spectra of: a) PEI, b) PEI after adsorption of CO_2, c) PEI heated at 85 °C in presence of air

It was concluded that the use of a steel support is not conducive to multiple use of polyamine as a CO_2 adsorbent. After using it three times, the adsorbent lost its properties. However, the described system can be used to study adsorption processes in an oxidizing environment or to study accelerated aging of polymers. The advantage of this setup is that the sorbent conducts heat very well and can react quickly to changes in temperature settings. A further development of this system will be conducted towards the use of a steel support including an intermediate layer of oxidation-resistant polymer, *e.g.* poly(carbonate urethane).

Similar behavior was observed for PEI covered 2 mm diameter glass spheres (Fig. 4, Table 2). Polyethyleneimine deposited on glass spheres adsorbed significant amounts of carbon dioxide only during the first process. The amount of captured CO_2 in the first run was 60% of that captured using polymer coated steel coils. The total surface area of the glass spheres bed was twice as large as the one of the metal coils. This means that part of the polymer was not accessible to the flowing air. Subsequent desorption at 85 °C in presence of air and sorption experiments showed lowered adsorption capabilities of the material. In the second run, the amount of adsorbed carbon dioxide dropped by more than a half. In the subsequent

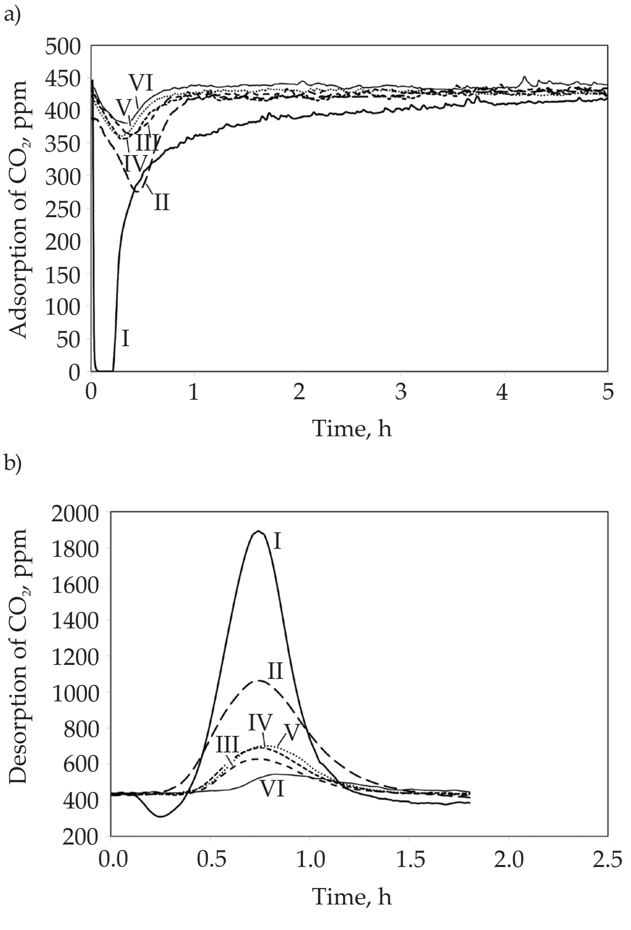


Fig. 4. Carbon dioxide: a) adsorption, b) desorption curves obtained for PEI polymer covered glass spheres; I–VI – numbers of adsorption/desorption cycles

T a b l e 2. Amounts of adsorbed and desorbed CO_2 for PEI deposited on glass spheres

Adsorption/ desorption cycle	Adsorption			Desorption		
	mg CO_2	mg CO_2/g of PEI	mg CO_2/g of adsorbent	mg CO_2	mg CO_2/g of PEI	mg CO_2/g of adsorbent
I	44.1	69.2	0.55	41.0	64.4	0.51
II	8.8	13.8	0.11	27.1	42.6	0.34
III	2.8	4.4	0.03	6.49	10.2	0.08
IV	4.7	7.4	0.06	9.9	15.5	0.12
V	0.9	1.5	0.01	10.4	16.3	0.13
VI	2.8	4.3	0.03	4.9	7.7	0.06

experiments, the decrease in sorption capacity was slower than for a steel coils support, but still not acceptable. The polymer washed out from the support showed similar properties to that removed from metal coils. The FT-IR spectrum was the same as shown in Fig. 3.

Based on previous experience, special attention has been paid to proper preparation of the fumed silica based sorbent. We avoided formation of small size grain fraction which was responsible for blockage of the air flow. Therefore, the sorbent was not mechanically treated after solvent evaporation. The low size grain fraction was removed on 0.25 mm sieves. Such a sorbent captured 4 to 6 times more carbon dioxide than the same material deposited on steel coils or glass sphere supports (Fig. 5, Table 3). 3 g of the adsorbent containing 1.5 g of PEI was capable of capture of all CO_2 from the air for up to 5 h which was equivalent to 210 dm^3 of the air. The theoretical maximum CO_2 capacity, taking into consideration the content of nitrogen in polyamine, for this adsorbent was 1.53 g CO_2. Data collected in Table 3 suggest that up to 40% of amine sites were involved in the process of carbon dioxide sorption. In case of metal coils and glass spheres these values were respectively 11 and 6.7%.

Repetition of the adsorption process four times did not reduce the amount of adsorbed carbon dioxide. The differences in Table 3 might come from measurement errors caused, *e.g.* by fluctuations in air humidity and carbon dioxide concentration in the air. The sorbent remained white after four cycles of adsorption/desorption except to the small fragment close to the air inlet, where its color

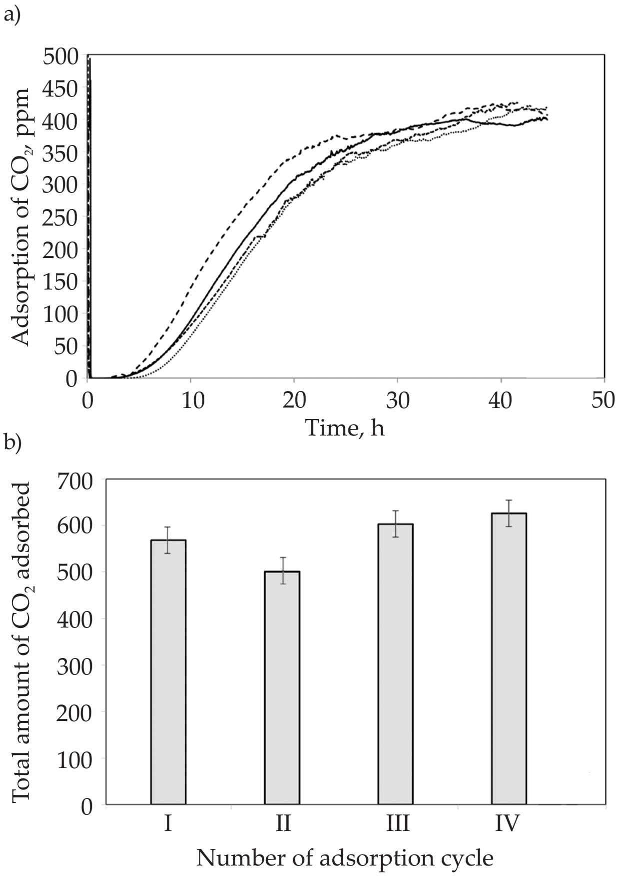


Fig. 5. a) Carbon dioxide adsorption curves, b) total CO_2 adsorbed amount for PEI polymer deposited on fumed silica (7 nm); I–IV – numbers of adsorption cycles

T a b l e 3. Amounts of adsorbed CO_2 for PEI deposited on fumed silica

Adsorption cycle	Adsorption					
	mg CO_2	mg CO_2/g of PEI	mg CO_2/g of adsorbent	Time h	Average relative humidity* %	Maximum relative humidity %
I	568	369	189	48	75	90
II	501	334	167	72	90	96
III	603	401	201	48	95	96
IV	626	417	209	48	93	96

* During first 5 hours.

changed to yellow. This indicates the possible oxidation of the polyamine, but this visible sign of decomposition did not affect the functioning of the sorption bed. Further experiments were carried out using fumed silica as a carrier for polymeric materials.

Polyglycerol A-HBPG based sorbents

The hyperbranched polyglycerol A-HBPG is a polymeric analogue of ethanoloamine, which is used in industrial CO_2 capture processes. It was synthesized in a two-step procedure involving ring opening co-polymerization of glycidol and epoxy derivative of phthalimide, followed by hydrazinolysis of phthalimide residues. Previous studies showed that it is possible to introduce up to 25% of amine containing repeating units to the structure of the polymer. This is equivalent to 4.408 wt % content of nitrogen in the polymer. Actual sample contained 4.205 ± 0.015 wt % of nitrogen which was in good agreement with the theoretical value. It is worth to stress out that the polymer contained only primary amine groups.

The adsorption experiments were performed for 12 h to assure complete saturation of the sorbent with CO_2. The adsorbent was prepared in analogy to the PEI/fumed silica sample, containing polymer and silica in the 1 to 1 mass ratio. However, the A-HBPG based adsorption bed showed twice as high (46 to 24 m^2/g) specific surface area in comparison to PEI bed. After each adsorption experiment a desorption took place at 85 °C for 3 h in the flow of air. The temperature was carefully controlled since desorption in temperatures above 100 °C introduced severe distortions to the CO_2 concentration measurements due to fast desorption of adsorbed moisture, which interferes with the FT-IR sensor installed in the HORIBA CO_2 analyzer.

It was observed that the adsorption capacity of the sorbent has dropped gradually in subsequent experiments. The changes are visible in Fig. 6 and Table 4 both for adsorption and desorption curves. After 12 adsorption/desorption cycles, the material lost approx. half of its CO_2 capacity. The possible reason for such behaviors was the oxidation of the polymer in presence of hot air.

Therefore, in further experiments the thermal desorption of CO_2 was performed under vacuum. Similar results could be obtained using heated neutral gas.

The data collected in Table 5 shows that the amounts of adsorbed CO_2 in all 17 experiments were on approximately the same level. The differences in the amount of adsorbed carbon dioxide are related to experiment condi-

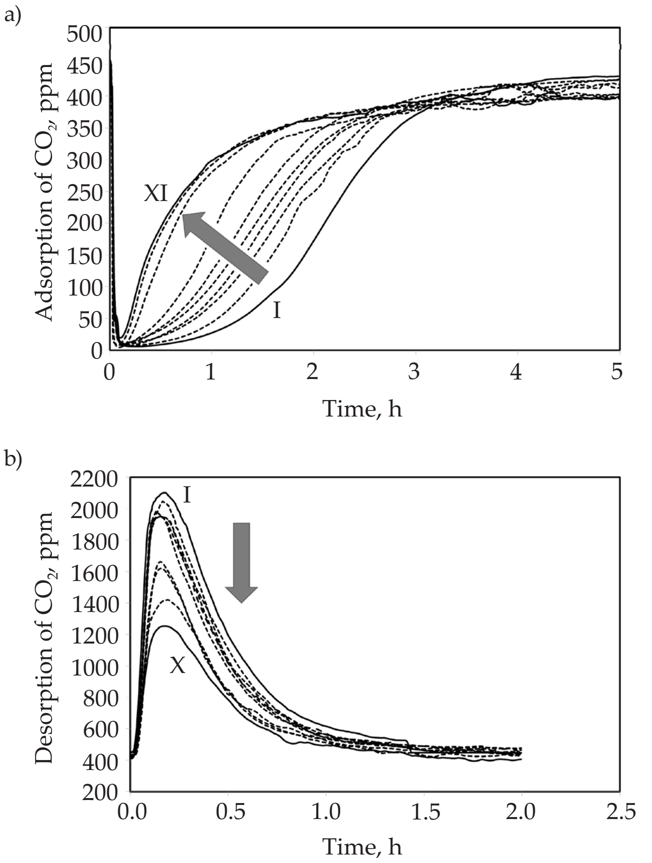


Fig. 6. Carbon dioxide: a) adsorption, b) desorption with hot air curves obtained for A-HBPG polymer deposited on fumed silica (7 nm); I, X, XI – numbers of adsorption/desorption cycles

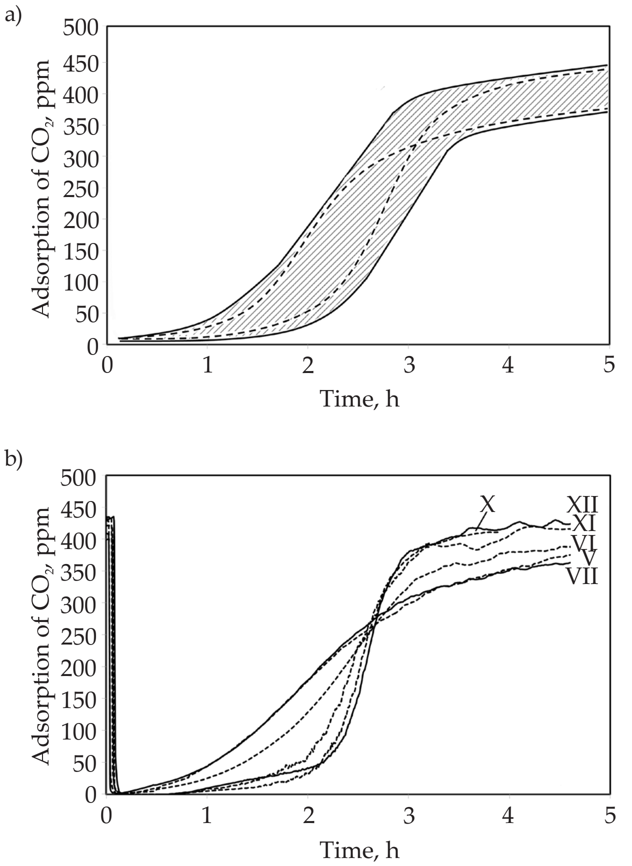


Fig. 7. Carbon dioxide adsorption curves obtained for A-HBPG polymer deposited on fumed silica (7 nm) (bed regenerated under vacuum): a) area representing the possible course of adsorption curves, b)sample adsorption curves; V, VI, VII, X, XI, XII – numbers of adsorption cycles

Table 4. Amounts of adsorbed and desorbed (in presence of hot air) CO_2 for A-HBPG deposited on fumed silica

Adsorption/ desorption cycle	Adsorption			Desorption		
	mg CO_2	mg CO_2/g of A-HBPG	mg CO_2/g of sorbent	mg CO_2	mg CO_2/g of A-HBPG	mg CO_2/g of sorbent
I	71.1	47.3	23.7	62.2	41.4	20.7
II	59.6	39.7	19.8	54.5	36.2	18.1
III	52.7	35.0	17.5	63.5	42.2	21.1
IV	64.4	42.9	21.4	53.6	35.7	17.8
V	53.7	35.8	17.9	51.4	34.2	17.1
VI	52.7	35.1	17.5	53.9	35.9	17.9
VII	48.2	32.1	16.0	57.7	38.4	19.2
VIII	56.8	37.8	18.9	53.7	35.7	17.9
IX	39.0	26.0	13.0	38.8	25.8	12.9
X	36.0	24.0	12.0	31.3	20.8	10.4
XI	35.4	23.6	11.8	39.6	26.3	13.2
XII	52.9	35.2	17.6	39.1	26.0	13.0

Table 5. Amounts of adsorbed CO_2 for A-HBPG deposited on fumed silica (bed regenerated under vacuum)

Adsorption cycle	Adsorption					
	mg CO_2	mg CO_2/g of A-HBPG	mg CO_2/g of adsorbent	Time, h	Average relative humidity*	Maximum relative humidity
I	71.1	47.7	23.9	12	49.8	73.8
II	86.9	58.4	29.2	12	46.3	92.2
III	97.5	65.5	32.8	12	59.2	96.7
IV	95.9	64.4	32.2	12	50.0	88.0
V	81.3	54.6	27.3	12	37.5	88.2
VI	80.2	53.9	26.9	12	49.1	94.3
VII	76.6	51.4	25.7	12	38.2	66.0
VIII	76.4	51.3	25.7	12	47.1	95.7
IX	82.7	55.5	27.8	12	78.3	95.7
X	85.8	57.7	28.8	12	78.9	96.1
XI	85.2	57.3	28.6	12	94.6	96.5
XII	83.2	55.9	27.9	12	95.4	96.7
XIII	82.6	55.5	27.7	12	92.7	97.0
XIV	81.3	54.6	27.3	12	84.7	95.0
XV	83.2	55.9	27.9	12	72.5	96.3
XVI	78.2	52.6	26.3	12	77.5	93.0
XVII	77.8	52.3	26.1	12	87.7	96.5

* During first 5 hours.

tions, mainly the relative humidity of the air. They were in most cases within a 5% inaccuracy level.

Figure 7 collects selected adsorption curves obtained during the 17 CO_2 adsorption experiments. The time scale in the figure is limited to 5 h while the whole experiments lasted 12 h. Due to the changing experiment conditions, mainly the relative humidity, the shape of the adsorption curve was in each case slightly different. The humidity is a variable that could change drastically several times during the adsorption experiment. The area visible in Fig. 7a represents all the possible ways of gaining maximum adsorption capacity of the bed observed in this experiment. The changing slope of the curves visible in Fig. 7b is most probably related to changing air humidity.

Figure 8 shows the comparison of the total amounts of adsorbed carbon dioxide in two experiments: when bed was regenerated with hot air (Fig. 8a) and when bed was regenerated under vacuum (Fig. 8b). In the first case the gradual decrease in adsorption capacity is observed. In the second case the decrease is not observed. Moreover, the overall maximum CO_2 capacity is higher in all cases

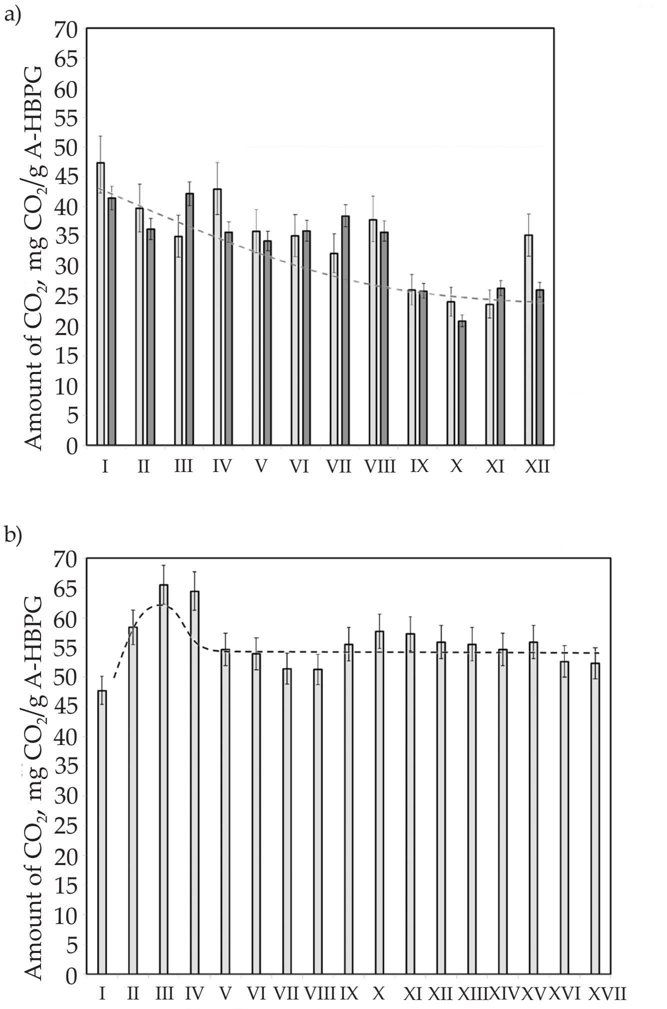


Fig. 8. a) The amounts of adsorbed and desorbed CO_2 in case of hot air regenerated adsorption bed, b) CO_2 adsorbed for vacuum regenerated adsorption bed

than adsorption levels seen in Fig. 8a. The levels of adsorbed CO_2 visualized in Fig. 7b suggest that the bed was being organized during the first few runs and then the "imprinted" structure remained stable.

3 g of the sorbent containing 1.5 g of A-HBPG was capable of capture of all CO_2 from the air for up to 2 h which is equivalent to 84 dm^3 of the air. The theoretical maximum CO_2 capacity, taking into consideration the content of nitrogen in polyglycerol for this sorbent was 0.198 g CO_2. Data collected in Table 5 suggest that up to 49% of amine sites were involved in the process of carbon dioxide sorption. It means that the efficiency of the use of amine groups in CO_2 capture for this sorbent was higher than that for PEI (40%). It can be explained by the larger specific surface area of the sorbent and increased mobility of the primary amine groups forming flexible structures together with methylene groups. Moreover, previous studies showed that amine containing repeating units are located mainly in the outer sphere of the macromolecules, which also makes them more accessible for CO_2.

CONCLUSIONS

The capability of the CO_2 adsorbent to be used in real-life systems depends on many factors. The properties of the sorbent are related to the materials used for its preparation, as well as the conditions during adsorption and desorption process. In addition, it should be stable over many adsorption–desorption cycles. In this article we reported preparation and characterization of several CO_2 adsorbents based on various supports and amine containing hyperbranched polyamines and polyglycerols. A-HBPG and PEI showed to be effective in CO_2 capture from the ambient air. Stability of the polymers under CO_2 adsorption/desorption conditions was investigated depending on the supports used for adsorbent preparation. Steel coils and glass sphere adsorbents have contributed to rapid decrease in CO_2 capture abilities of the adsorbent. Adsorbents consisting of A-HBPG or PEI and fumed silica in the 1 to 1 mass ratio were capable of adsorbing significant amounts of carbon dioxide; up to 97.5 mg and 626 mg, respectively which was equivalent to the involvement of 49 and 40% of nitrogen atoms present in the sample in the adsorption process. The investigated CO_2 adsorbents could be regenerated upon by heating. Desorption took place at 85 °C. The A-HBPG containing adsorbents were capable of multiple CO_2 adsorption/desorption sequences without the change of adsorption capability, provided that the desorption process was carried out in the absence of oxygen. Amine containing hyperbranched polymers due to their high selectivity for CO_2, fast adsorption kinetics, low glass transition temperatures and amorphous structure are promising materials for CO_2 capture.

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