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Deodorization of model biogas by means of novel non-ionic deep eutectic solvent

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Abstract: The paper presents new non-ionic deep eutectic solvent (DES) composed of natural and non-toxic components i.e. guaiacol, camphor and levulinic acid in 1:1:3 molar ratio as a promising absorbent for removal of selected volatile organic compounds (VOCs) including dichloromethane, toluene, hexamethyldisiloxane and propionaldehyde from model biogas.

The affinity of DES for VOCs was determined as vapour-liquid coefficients and the results were compared with several well-known DESs based on quaternary ammonium salt as well as n-hexadecane and water. For new DES, the absorption process was carried out under dynamic conditions.

The results indicate that non-ionic DES has high affinity and capacity for VOCs being comparable to n-hexadecane. In addition, absorbed VOCs could be easily desorbed from DES using activated carbon and absorbent could be re-use minimum five times without significant loss of absorption capacity.

Introduction

Biogas from wastewater treatment plants and landfill sites consist of 30–60% v/v methane, 15–30% v/v carbon dioxide, 5–20% v/v nitrogen, 1–10% v/v oxygen and about 1–2% v/v of other contaminants including hydrogen sulfide, ammonia and numerous volatile organic compounds (VOCs), i.e. aliphatic and aromatic hydrocarbons, siloxanes, volatile organosulfur and organohalogen compounds, and oxygenated organic compounds (Rasi et al. 2007). Impurities from biogas can have environmental impacts such as stratospheric ozone depletion, the greenhouse effect, and reduction in local air quality as well as effect damage to power equipment. In addition, the presence of odour compounds resulting from biogas production is a serious problem, especially for residents of areas immediately adjacent to production plants (Kozłowski et al. 2019; Szulczyński et al. 2017).

Currently, various technologies have been developed for the deodorization of biogas stream, i.e. chemical and physical absorption, adsorption, condensation, membrane separation, thermal or catalytic oxidation, biological treatment, biofiltration (Miller et al. 2018, 2019; Wieczorek et al. 2012) and advanced oxidation process (Baena-Moreno et al. 2019). Among the technologies, physical absorption is one of the most attractive technologies due to its simplicity, economical, safety, and its potential high efficiency for the removal of medium or high VOCs concentration from the gas phase. The most important parameter during the absorption process is the use of a suitable absorption solvent. Absorbents should be characterized by high absorption capacity of VOCs, low vapor pressure, high-boiling point, high diffusion coefficient, low price, safety, and no toxicity. Some common solvents that may be useful for the removal of odorous compounds include water, mineral oils, alcohols, ketones, and amines (Noorain et al. 2019).

In recent years, in accordance with the principles of green chemistry, conventional absorbents have been replaced by new generation green solvents. Until recently, the studies have been focused on the application of ionic liquids (ILs) as absorbents due to their unique properties. However, several reports have pointed out the problems with biodegradability, high toxicity, difficult and expensive synthesis of most ILs (Romero et al. 2008). To overcome the disadvantages of ILs, eco-friendly solvent system named as deep eutectic solvents (DESs) was introduced (Abbott et al. 2003). The DESs are mixture mainly composed of two or three non-toxic and biodegradable compounds with a melting point lower than its individual components. Until now, DESs have been widely used in catalysis, analytical chemistry, separation processes and electrochemistry, water and air purification (Tang et al. 2015, Makoś et al. 2018, Makoś et al. 2018).

There are currently several reports in which DESs have been successfully used to remove inorganic impurities from the gas phase, i.e. water, carbon dioxide, sulfur dioxide, ammonia and hydrogen sulfide (Chen et al. 2019, Duan et al. 2019). To the best of our knowledge, only one study focused on the application of deep eutectic solvents for VOCs absorption. In this study, authors tested several DESs composed of choline chloride with

urea and with ethylene glycol, glycerol and levulinic acid in 1:2 molar ratio, mixtures composed of tetrabutylphosphonium bromide with glycerol (1:1 molar ratio), and with levulinic acid (1:6 molar ratio) as well as tetrabutylammonium bromide with decanoic acid in 1:2 molar ratio for absorption of toluene, acetaldehyde and dichloromethane (Moura et al. 2017). In studies, the DESs present similar absorption capacities for acetaldehyde (corresponding to 99.9% absorption of the initial VOC amount). Due to the high absorption potential of DESs, they can be used as an alternative to conventional organic solvents used for VOC absorption from a gas stream.

The paper discusses the novel non-ionic DESs based on a combination of ±camphor [C], guaiacol [G] and levulinic acid [Lev] in 1:1:3 molar ratio. The affinity of new DESs for selected VOCs including toluene (T), dichloromethane (DCM), hexamethyldisiloxane (HMDS) and propionaldehyde (PA) was determined and the results were compared with several well--known DESs based on quaternary ammonium salts as well as n-hexadecane and water. For new DES, the absorption process was carried out under dynamic conditions. The reusability and regeneration of DESs were also investigated.

Experimental

Materials and reagents

Camphor, guaiacol, levulinic acid, propionaldehyde, toluene, dichloromethane, hexadecane, hexamethyldisiloxane, choline chloride, urea, and diethylene glycol (purity ≥ 95%) were purchased from Sigma-Aldrich (USA). Compressed gases were used for the preparation of model biogas and chromatographic analysis such as nitrogen (purity N 5,5), air (purity N 5.0) generated by a DK50 compressor with a membrane dryer (Ekkom, Poland) and hydrogen (purity N 5.5) generated by a 9400 Hydrogen Generator (Packard, USA).

Procedures

Preparation and physicochemical properties of DESs

New non-ionic DESs, as well as ionic DESs, were synthesized by mixing [C], [G] and [Lev] in a 1:1:3 molar ratio and choline chloride [ChCl] with urea [U], diethylene glycol [DEG], and levulinic acid in 1:2 molar ratio. The eutectic mixtures were stirred magnetically at 60°C until homogeneous liquids were obtained. The liquids were then left to cool spontaneously to room temperature. Dynamic viscosity and density were measured over a wide range of temperature from 25 to 50°C which is the usual absorption tower operating temperature range. The viscosity was determined using BROOKFIELD LVDV-II+ viscometer (Labo--Plus, Poland). The density was measured by means of DMA 4500 (Anton, Paar, Poland). The determination of dynamic viscosity, and density of DESs were performed at atmospheric pressure.

Affinity of absorbents for the selected VOCs

The affinity of absorbents for VOCs was evaluated by means of vapor – liquid partition coefficients (K) defined as (1):

$$K = \frac{C_G}{C_L} \tag{1}$$

Where: C_G – concentration of VOCs in the gas phase in the equilibrium with a liquid solution of concentration C_L in the solute. Affinity tests were carried out in 20 ml glass vials containing 1 ml of absorbents enriched with 50 ppm v/v of each VOCs. The vials were closed with PTFE-coated silicone rubber septa and sealed with aluminum caps. The vials were maintained in laboratory shaker at 25 and 50°C for 48 h. The concentration of VOCs in gas phase was determined using static headspace coupled to gas chromatography (HS-GC). The concentration of VOCs in liquid phases was calculated from a mass balance on the VOC after determination of VOCs in the gas phases. The measurements were carried out using gas chromatograph Autosystem XL equipped with flame ionization detector (FID) (PerkinElmer, USA), an HP-5 (30 m × 0.25 mm × 0.25 µm) capillary column and TurboChrom 6.1 software. The following conditions were used for the GC-FID analysis: injection port temperature 200°C, injection mode: split (15:1), detector temperature 320°C, detector gases flow rates: air 450 mL/min, hydrogen 45 mL/min, carrier gas (nitrogen) flow rate 2 mL/min and oven temperature 60°C.

Absorption process

The model biogas, as well as the absorption process, was prepared by means of the bubbling phenomenon. Nitrogen was passed through a 20-mL vial containing 1 mL of each VOCs. The formed mixture was diluted with a nitrogen stream to achieve the desired concentration of VOCs (50 ppm v/v) in the model biogas mixture. The nitrogen containing VOCs was passed through a 60-mL absorption column containing 50 mL of DES. The total flow of nitrogen and gaseous VOCs was kept constant at 50 mL/min. The concentration of VOCs was monitored at the inlet and outlet of the bubble column using GC-FID. The processes were carried out for 3000 minutes. The absorptivity (A) of VOCs in the DES was calculated using equation (2):

$$A = \frac{C_{in} - C_{out}}{C_{in}} \tag{2}$$

Where: C_{in} – VOCs concentration of the inlet gas (ppm v/v), and C_{out} – VOCs concentration of the outlet gas (ppm v/v).

Regeneration and reusability of DES

After the absorption process, the VOCs absorbed in the DES were removed by means of adsorption with activated carbon. The DES containing VOCs was mixed with activated carbon in a glass vial and subsequently filtered using a PTFE – syringe filter with a pore size of 0.22 µm to ensure the complete removal of the activated carbon from the absorbent phase. The concentration of VOCs in DES was controlled using HS-GC-FID procedure described above. The absorption/desorption cycles were repeated five times.

Results and discussion

Physicochemical properties of new DES

In the first stage of research, the volatility of DES was studied by passing nitrogen through the new absorbents at two temperatures – 25 and 50°C. The gas phase after bubbling DES was analyzed by GC. No peaks were observed in the chromatogram, indicating a lack of DES volatility at the studied temperatures.

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It is well-known that the viscosity and density of absorbents play an important role in the mass transfer process. The viscosity and density were highly affected by the nature of DES components and temperature. The density of new DES at 25°C (1.1123 g/cm^3) as well as DESs composed of ChCl and urea (1.2001 g/cm^3), levulinic acid (1.1371 g/cm^3), and diethylene glycol (1.1143 g/cm^3) are higher than conventional absorbents, i.e. hexadecane (0.7701 g/cm^3) and water (0.9970 g/cm^3), and they are decreasing with increasing temperature (Figure 1A).

The viscosity of new DES is lower compared to the viscosity of the most popular DESs and slightly higher compared to viscosity values of organic solvents (e.g. n-hexadecane which represent mineral oil and water) already used for the removal of VOCs from the gas phase.

Deodorization of VOCs from model biogas

A key feature for deodorization of biogas is the VOCs affinity for DESs. Table 1 summarized the vapor-liquid partition coefficients of four VOCs in new non-ionic DES, and the most popular ionic DESs as well as water and n-hexadecane.

The significant decrease in vapor-liquid partition coefficients for the studied absorbents, compared to water, indicates that a greater amount of selected VOCs are solubilized in these absorbents. All VOCs showed similar K values in DES composed of [G][C][Lev] (1:1:3) than those obtained for n-hexadecane which is one of the most common organic solvents used for the removal of VOCs from gas phases. The partition coefficient values obtained for PA as well as for DCM are in the same order of magnitude than those observed for the other choline chloride-based DESs. For the T and HMDS, non-ionic DES ([G][C][Lev]) is the most effective absorbent, due to the lowest K values. Higher K values for PA were obtained using all DESs compared to water and n-hexadecane, which indicates a lower efficiency of DES absorption for compounds from the aldehydes group. Similar K values (higher than [G][C][Lev] (1:1:3) and n-hexadecane) were obtained for most VOCs using DES containing [ChCl] in their structure. This is probably due to the limited solubility of VOCs in [ChCl]. However, these results are lower than those for water, which indicates better sorption properties of ionic DESs. The partition coefficient values for most VOCs in DESs are comparable in 25°C and 50°C. This trend is very important for the industrial use of environmentally friendly solvents as absorbents because the temperature of the biogas stream generated in the industry is not always stable. At 25°C, the higher absorption efficiency of VOCs was observed, while at 50°C, lower absorption efficiency was noted. At higher temperatures, lower viscosity of absorbents is observed, which theoretically should increase the absorption capacity. On the other hand, higher temperatures may adversely affect the affinity of VOC for DES, which strongly depends on hydrogen bonds, electrostatic interactions, as well as $\pi - \pi$ interactions, which are probably reduced. The interaction of both effects affects similar affinity values of VOCs to DES

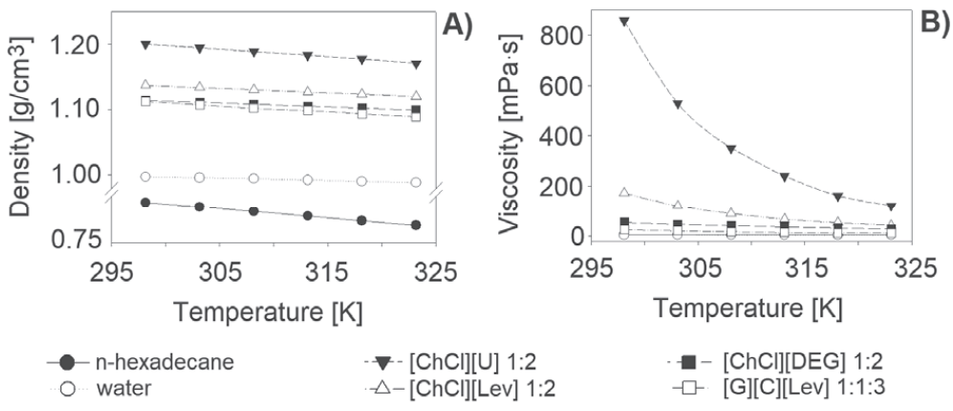

Fig. 1. A) Densities for absorbents as a function of temperature, B) Viscosities for absorbents as a function of temperature

Table 1. Vapour–liquid partition coefficients (K) of VOCs in absorbents at 25 and 50°C.

Absorbent	T		PA		DCM		HMDS	
	25°C	50°C	25°C	50°C	25°C	50°C	25°C	50°C
[G][C][Lev] (1:1:3)	<0.001	0.017	0.008	0.019	0.057	0.044	<0.001	<0.001
[ChCl][U] (1:2)	0.026	0.157	0.010	0,025	0.052	0.208	0.012	<0.001
[ChCl][Lev] (1:2)	0.035	0.091	0.011	0.026	0.075	0.081	0.0085	0.012
[ChCl][DEG] (1:2)	0.076	0.168	0.010	0.025	0.038	0.103	0.0096	0.018
n-hexadecane	<0.001	0.014	0.009	0.012	0.077	0.086	<0.001	<0.001
water	0.203	0.609	0.0045	0.015	0.112	0.251	0.61	0.86

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in 25 and 50°C. The lower differences in the viscosity of absorbents in the temperature range, the greater the stability of the absorption process were observed.

In a dynamic system, two other parameters, i.e. flow rates and the volume of absorbent also have a significant influence on absorption efficiency. The studies were conducted under model conditions using nitrogen to verify only the interactions between VOCs and the new DES. In the studies, the effect of different flow rates between 20 and 70 mL/min were tested (Figure 2A). In the industrial point of view, the flow rate of contaminated biogas should be as high as possible. However, the results indicated that at a higher flow rate (above 50 mL/min), the absorption efficiency of VOCs was significantly decreased. Hence, 50 mL/min was chosen as the optimum flow rate by the proposed method. In the next step, the volume of absorbent between 15 and 50 mL was investigated (Figure 2B).

The results showed that with the increase in DES volume, the absorption capacity increased significantly and the time of complete saturation of DES increased from 950 min to 3000 minutes. The VOCs absorption capacity of DES was investigated for 50 ppm v/v concentration. Optimization studies for all compounds came out at a similar level. That is why the paper presents only the most representative graphs obtained for T.

Figure 3 presents the absorption capacity of DES in optimum process conditions. The results indicate that the absorption capacity strongly influences the structure of VOCs. After 1200 minutes, DES was completely saturated with DCM and PA compounds. While at that time, the absorption capacity for toluene and HMDS was 0.26 and 0.52 respectively. The T and HMDS removal process could continue for 1800 minutes. The results are consistent with the vapor-liquid partition coefficient values. This indicates that the new DES can more effectively remove volatile siloxane compounds and aromatic hydrocarbons from the biogas stream.

Regeneration and reusability of DES

Regeneration and reusability of the DES for multiple uses as an absorbing solvent for VOCs removal are important in economics (Figure 4). In the studies, adsorption process based on activated carbon was applied to remove VOCs from DES. The results indicate that VOCs could be completely removed from DES and absorbent could be re-used minimum five times without significant loss of absorption capacity.

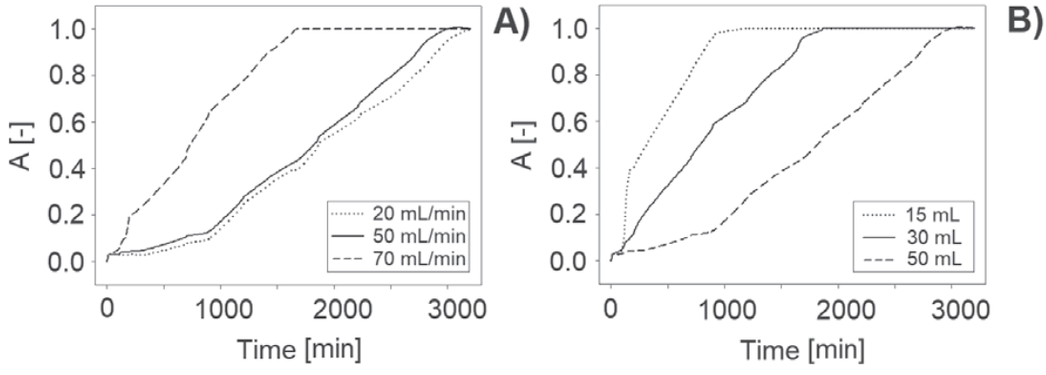

Fig. 2. Experimental breakthrough curves of T absorption with [G][C][Lev] (1:1:3 molar ratio) at different: A) flow and B) volume of DES

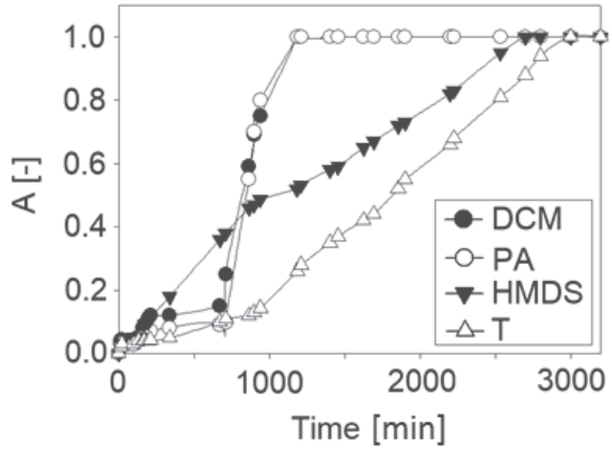

Fig. 3. VOCs absorption curves in [G][C][Lev] (1:1:3 molar ratio) at optimum conditions (25°C, 50 mL of DES, gas flow rate 50 mL/min, initial concentration of VOCs 50 ppm v/v)

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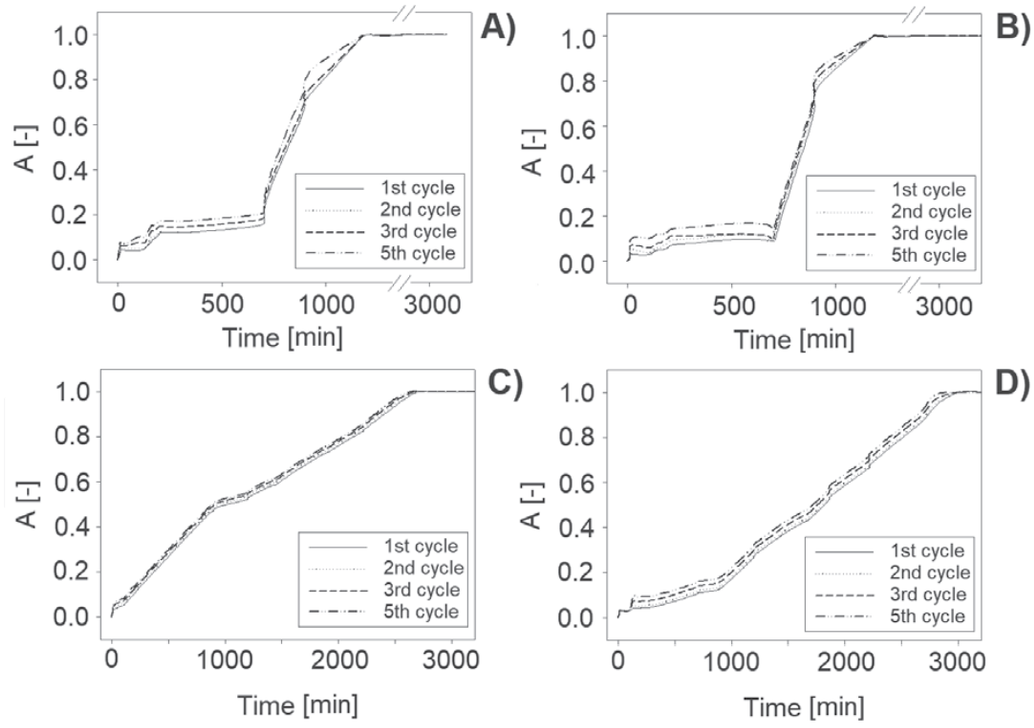

Fig. 34. Reusability of[G][C][Lev] (1:1:3 molar ratio): A) PA B) DCM C) HMDS D) T

Conclusions

The paper shows the new DES composed of natural non-toxic components including camphor, guaiacol and levulinic acid in 1:1:3 molar ratio as a promising candidate for implementation in the absorption process for the removal of VOCs from model biogas. The new DES confirms the high affinity and capacity for T, PA, DCM, and HMDS being comparable to n-hexadecane or higher than typical DESs composed of quaternary ammonium salts. In addition, the absorbed VOCs could be easily desorbed from DES using activated carbon and the absorption capacities are stable after five cycles. The obtained results indicate the great potential of the use of DES for the purification of real biogas streams.

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Dezodoryzacja modelowego strumienia biogazu z użyciem nowej niejonowej cieczy eutektycznej

Streszczenie: W pracy przedstawiono nową niejonową ciecz eutektyczną (DES) złożoną z naturalnych i nietoksycznych składników tj. gwajakol, kamfora i kwas lewulinowy w stosunku molowym 1:1:3, jako obiecujący absorbent do usuwania wybranych lotnych związków organicznych w tym dichlorometanu, toluenu, heksametylodisiloksanu oraz aldehydu propionowego.

W celu określenia powinowactwa DES do LZO, wyznaczono współczynniki podziału ciecz–para. Uzyskane wyniki porównano z popularnymi DES zawierającymi w strukturze czwartorzędową sól amoniową, a także z n-heksadekanem oraz wodą.

Dla nowej DES, proces absorpcji przeprowadzono również w warunkach dynamicznych. Wyniki wykazały, że nowa niejonowa DES charakteryzuje się dużym powinowactwem do wybranych LZO oraz dużą pojemnością sorpcyjną, a parametry te są porównywalne do n-heksadekanu.

Dodatkowo, zaabsorbowane LZO mogą być łatwo desorbowane przy użyciu węgla aktywnego. Dzięki temu, absorbent w postaci DES może być użyty minimum pięć razy bez znaczącego zmniejszenia pojemności sorpcyjnej.

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