



Treatment with activated carbon and other adsorbents as an effective method for the removal of volatile compounds in agricultural distillates

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ABSTRACT

This study investigates the effect of treatment with activated carbon and other adsorbents on the chemical composition and organoleptics of a barley malt-based agricultural distillate. Contact with activated carbon is one of the methods by which the quality of raw distillates and spirit beverages can be improved. Samples placed in contact with 1 g activated carbon (SpiritFerm) per 100 ml distillate with ethanol content of 50% v/v for 1 h showed the largest reductions in the concentrations of most volatile compounds (aldehydes, alcohols, esters). Increasing the dose of adsorbent to over 1 g 100 ml⁻¹ did not improve the purity of the agricultural distillate significantly. Of the tested compounds, acetaldehyde and methanol showed the lowest adsorption on activated carbon. The lowest concentrations of these congeners (expressed in mg l⁻¹ alcohol 100% v/v) were measured in solutions with ethanol contents of 70–80% v/v, while solutions with an alcoholic strength by volume of 40% did not show statistically significant decreases in these compounds in relation to the control sample. The reductions in volatile compounds were compared with those for other adsorbents based on silica or activated carbon and silica. An interesting alternative to activated carbon was found to be an adsorbent prepared from activated carbon and silica (Spiricol). Treatment with this adsorbent produced distillate with the lowest concentrations of acetaldehyde and isovaleraldehyde, and led to the greatest improvement in its organoleptics.

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Introduction

Volatile compounds in agricultural distillates (raw spirits), including carbonyl compounds, esters, acids and alcohols, are to varying degrees responsible for the organoleptics of distillates. They may originate partially from the raw materials, or may be byproducts formed during alcoholic fermentation and distillation (Balcerek, Pielech-Przybylska, Dziekońska-Kubczak et al. 2016). Some of these compounds, such as methanol (Paine & Davan 2001) and acetaldehyde (IARC 1999), can, in excessive quantities, have adverse effects on human health. Drinking spirits with high levels of higher alcohols may furthermore lead to increased incidence of liver disease (Lachenmeier et al. 2008). While the main cause of hangover symptoms is ethanol, congeners can increase the severity of veisalgia (Rohsenow & Howland 2010; Sales et al. 2010). It is therefore considered preferable to

remove these substances from beverages (Stephens et al. 2008).

One of the methods for improving the quality of raw distillates and spirit beverages is contact with activated charcoal (Ng et al. 1996; Mukhin et al. 2009), or with other adsorbents such as aluminosilicates, bentonite or natural clay (Cantanhede et al. 2005; Cantão et al. 2010; Zacaroni et al. 2015). These adsorbents eliminate a portion of the volatile compounds in the ethanol solution, as well as triggering the catalysis of a number of chemical reactions, such as oxidation, esterification, isomerisation and hydration (Wang & Peng 2009). Siliceous adsorbents with chemically bonded phases (CBPs) are the most commonly used adsorbents in chromatography. CBPs are also used in the preparation of a broad range of food matrices (water, waste water, blood, urine, plant, fruit extracts, etc.) for solid-phase extraction (SPE) (Unger 1990).

Adsorption capacity cannot easily be predicted, since it depends on a range of factors. These include the properties of the adsorbent (porosity, surface area, particle size) and of the adsorbate (structure, water solubility, ionic charge, functional groups, polarity, functionality, molecular weight and size). Adsorption capacity also depends on the solution conditions (solvent, pH, temperature, ionic strength, solute concentration and competition between solutes), on the interactions at the solid-liquid interface and on the type of experimental set-up (Soto et al. 2011).

Activated carbon (AC) is a strongly adsorbent and hydrophobic material (Ligor et al. 1998). Its adsorbent properties depend on its composition, physicochemical properties and mechanical strength (Antal & Grønli 2003). The surface of AC can expand to more than $2500 \text{ m}^2 \text{ g}^{-1}$, while the minimum surface area for a preparation to be classified as a sorbent is $50 \text{ m}^2 \text{ g}^{-1}$ (Stelmach 2008). ACs are not classified as dangerous substances under either European Union Directive 67/548/EC (Dangerous Substances) or Directive 91/155/EC (Dangerous Preparations), nor by their relevant amendments (respectively 2001/59/EC and 2001/60/EC).

The properties of AC enable it to be used in many different technological processes associated with drinking water, food, alcoholic beverages, medicine and other products. It is used to trap very volatile compounds. For instance, AC has been employed for processing industrial wastewater containing phenols, and for removing coloured substances from juices (Carabasa et al. 1998; Arslanoğlu et al. 2005), as well as for removing contaminants and purifying fermentation products, including food additives, pharmaceuticals, antibiotics, vitamins, steroids and biosurfactants (Dubey et al. 2005). In order to avoid browning and over-oxidation of phenolic compounds in bottled white wines, the oenological industry bonds polyphenols to ACs, bentonite, casein, yeasts and food-grade polymers (Spagna et al. 1999; Corcho-Corral et al. 2005; Muñoz-González et al. 2009). The use of AC can improve the balance of fermentation byproducts in spirit beverages, such as vodka, with perceptible improvements in organoleptic properties (Siříštová et al. 2012). However, the treatment of

spirits with this adsorbent removes both undesirable compounds and compounds that are desirable in terms of taste and fragrance. This can be especially important in the production of spirits such as whisky or vodka (Balcerek, Pielech-Przybylska, Strąk et al. 2016).

An important factor determining the quality of ACs is their ash content. A high ash content can be an indication of calcium, aluminium, manganese or iron accumulation on the AC. Such deposits reduce the overall activity of the AC and the efficiency of reactivation. The metal oxides (e.g., Fe_2O_3) can leach out of the AC, resulting in discoloration. A carbon with a low soluble ash content should be used to avoid heavy metal poisoning and excess algal growth (Desotec 2016). ACs derived from a demineralised parent coal possess greater mechanical strength and nearly double the surface area of those produced without demineralisation (Allen & Whitten 1998).

The simplest setup for the adsorption of substances on activated charcoal involves stirring a quantity of charcoal into ethanol solution. The process is terminated by filtering the solid particles. The amount of activated charcoal required and the duration of treatment needed depend on the type and quality of the charcoal (Siříštová & Melzoch 2009). Another possibility is to filter the ethanol solution through a large amount of activated charcoal packed in a contact column or several columns in series. The solution is passed through the columns at a rate that ensures sufficient contact with the solid and liquid phases (Dudetskij et al. 2001; Eliseev et al. 2006).

There are few reports in the literature on the effect of adsorbent type and process parameters on the efficiency of congener removal from alcoholic solutions. The aim of our study was to evaluate the effectiveness of treatment with AC for the purification of agricultural distillate. We observed changes in the qualitative and quantitative composition of the volatile compounds in a barley malt-based distillate, and to its sensory characteristics. The scope of the experiments included determining the effects of adsorbent dose and ethanol content on the concentrations of volatile congeners in the distillate and its organoleptic characteristics. Moreover, we compared the results with those for other sorbents based on silica or AC and silica.

Materials and methods

Materials

The raw material used was a barley malt-based agricultural distillate produced on an industrial scale by a Polish distillery (PPHU Zbig-Rol, Prusinowice, Poland), with an alcoholic strength by volume (ASV) of 93.5% v/v. The distillate was treated using the following commercial sorbents:

- SpiritFerm-activated carbon (particle diameter 0.4–0.85 mm, surface area: 1000–1100 m² g⁻¹) (SpiritFerm, Sweden).
- Spiricol preparation (granular adsorbent based on AC and silicon dioxide) (Erbslöh, Germany).
- DistiPur preparation (mineral adsorbent granules based on silicon dioxide) (SpiritFerm).

Doses of adsorbents were decided taking into account supplier guidelines.

Preparation of samples

To determine the effect of the dose of AC on the changes in the concentrations of volatile impurities, AC (SpiritFerm) was added in doses of 0.5, 1.0 and 2.0 g to 100 ml to samples of diluted agricultural distillate. The distillate was diluted with deionised water from an initial ASV of 93.5% to 50% v/v. The samples were placed in glass bottles, sealed and stirred for 1 min at 10-min intervals. The total contact time between the AC and the alcoholic solution was 1 h. The experiments were conducted at the natural pH of the solution and at RT. At the end of the contact time the solutions were filtered through filter paper in a Buchner funnel.

To assess the effect of ethanol content on the adsorption of chemical impurities, samples of the agricultural distillate diluted to ASVs of 40% v/v, 50% v/v, 60% v/v, 70% v/v and 80% v/v were prepared. Next, 100 ml of each solution were transferred to glass bottles, and 1 g of SpiritFerm-AC was added to each bottle. The subsequent stages of the procedure were the same as those described above for testing the effect of the dose of AC.

The results from processes using SpiritFerm-AC were compared with those with other adsorbent materials, Spiricol (granular adsorbent based on AC and silicon dioxide) and DistiPur (mineral granulated adsorbent based on silicon dioxide). Experiments were conducted using Spiricol and DistiPur in 1 g per 100 ml doses, and using distillate with 50% v/v ethanol content. As described above, the alcoholic solutions and adsorbents were stirred in bottles for 1 min at 10-min intervals, with a total contact time of 1 h. Finally, the solutions were passed through filter paper in a Buchner funnel.

Table 1 shows the design of experiments for the treatment of agricultural distillate with AC and other adsorbents.

The control sample for each set of experiments was the agricultural distillate before treatment. All samples were subjected to chromatographic and organoleptic analysis.

Analytical methods

Analysis of major volatile compounds (GC-FID)

Analysis of the major volatile compounds was performed using GC. GC-FID analysis was conducted on an Agilent 7890A GC (Santa Clara, CA, USA), equipped with an FID, a split/splitless injector and a capillary column (HP-Innowax, 60 m × 0.32 mm

Table 1. Design of experiments for the treatment of agricultural distillate with activated carbon and other adsorbents.

| Number of sets | Assessed parameter | Adsorbent type | Adsorbent dose (g 100 ml ⁻¹) | Ethanol content in tested solution (% v/v) | Contact time (h) |
|----------------|-------------------------------|-----------------------------|--|--|------------------|
| 1 | Dose of activated carbon | SpiritFerm-activated carbon | 0.5 | 50 | 1 |
| | | SpiritFerm-activated carbon | 1.0 | 50 | 1 |
| | | SpiritFerm-activated carbon | 2.0 | 50 | 1 |
| 2 | Ethanol content in solution | SpiritFerm-activated carbon | 1.0 | 40 | 1 |
| | | SpiritFerm-activated carbon | 1.0 | 50 | 1 |
| | | SpiritFerm-activated carbon | 1.0 | 60 | 1 |
| | | SpiritFerm-activated carbon | 1.0 | 70 | 1 |
| | | SpiritFerm-activated carbon | 1.0 | 80 | 1 |
| | | SpiritFerm-activated carbon | 1.0 | 80 | 1 |
| 3 | Comparison of adsorbents type | DistiPur preparation | 1.0 | 50 | 1 |
| | | Spiricol preparation | 1.0 | 50 | 1 |
| | | SpiritFerm-activated carbon | 1.0 | 50 | 1 |

inner diameter \times 0.50 μm film thickness; Agilent). Each sample was injected (1 μl) using an autosampler in split mode (1:45). The temperature of the injector and FID was kept at 250°C. The oven temperature programme was as follows: 40°C initial, 6 min hold; 2°C min^{-1} to 80°C; 5°C min^{-1} to 210°C final, 5 min hold. The flow rate of the carrier gas (helium) through the column was 2 ml min^{-1} . The volatile compounds (acetaldehyde, ethyl acetate, methanol, propanol, isobutanol, butanol, amyl alcohols, pentanol, hexanol and 2-phenylethanol) were identified using reference GC standards. The volatile compounds were quantified with reference to standard calibration curves, using 4-heptanone as the internal standard. The data were analysed using MassHunter software (Agilent).

Minor volatile compounds analysis (SPME-GC-MS)

Chromatographic analysis of minor volatile compounds in the distillates was performed using a GC apparatus (Agilent 7890A) with an MS (Agilent MSD 5975C). Solid-phase microextraction (SPME) was used to extract the volatile compounds, with subsequent analysis using GC-MS.

SPME conditions: a 5 ml spirit sample (diluted to 20% v/v ethanol concentration) mixed with the internal standard (4-heptanone at a concentration of 45 mg per ml of absolute alcohol) was placed in a 20 ml amber headspace vial and capped tightly. Carboxene/divinylbenzene/polydimethylsiloxane fibre (DVB/CAR/PDMS, 50/30 μm , 1 cm fibre length; Supelco, Bellefonte, PA, USA) was used in the analysis of all samples. The vial was equilibrated at 50°C for 15 min, after which SPME fibre was introduced. Extraction was continued for 15 min at 50°C. The compounds were then desorbed for 5 min at 250°C in split mode (1:10). GC-MS analysis was performed. After each injection, the fibre was conditioned at 250°C for 10 min. All headspace SPME extractions were performed in triplicate.

SPME-GC-MS conditions: a capillary column (VF-WAX MS, 60 m \times 0.32 mm inner diameter \times 0.50 μm film thickness; Agilent) was used to separate the compounds. The GC oven temperature programme was as follows: 35°C initial, 6 min hold; 2°C min^{-1} to 80°C; 10°C min^{-1} to 250°C final, 5 min hold. The flow rate of the carrier gas (helium) was 1.2 ml min^{-1} . The MS run parameters were as follows: ion-source temperature 230°C, transfer line

temperature 260°C, quadrupole temperature 150°C, ionisation energy 70 eV. The volatile components were identified based on a comparison of their mass spectra with those registered in the NIST MS library (NIST 98.1 and the Wiley Registry of Mass Spectral Data, 8th edn). Their retention indices (RI) were also compared with reference compounds and with data in the literature (Chida et al. 2004; Mahattanatawee et al. 2005). The volatile compounds were quantified using MassHunter software (Agilent).

All GC standards were purchased from Sigma Aldrich (St. Louis, MO, USA) and were of GC purity. Standard solutions were prepared using anhydrous ethanol (Sigma-Aldrich) as the solvent and refrigerated at 4°C during storage.

Sensory analysis

Sensory assessment of the samples of agricultural distillate (previously diluted to ASV of 40%) was performed by seven panellists using the Buxbaum model of positive ranking (Tešević et al. 2005). This model is based on a rating of four sensory experiences, with a maximum score of 20 points overall. Points are given for colour (0–2), clearness (0–2), aroma (0–4) and taste (0–12).

Statistical analysis

All samples were prepared and analysed in triplicate. Statistical analyses were performed using STATISTICA 10 software (Statsoft, USA). Fisher's least significant difference (LSD) post-hoc test was used at a significance level of 0.05 to verify statistical differences.

Results and discussion

Effectiveness of purification of agricultural distillate by AC and other adsorbents

Effect of AC dose

When assessing the effect of the amount of AC on the adsorption of volatile congeners from the agricultural distillate (Table 2), it was observed that a dose of adsorbent between 0.5 and 2 g per 100 ml of distillate removed different volatile compounds with different degrees of efficiency.

Table 2. Effect of the dose of SpiritFerm-activated carbon (ethanol concentration 50% v/v, contact time of 1 h) on concentration of volatile compounds in agricultural distillate samples.

| Compound (mg l ⁻¹ alcohol 100% v/v) | Control sample | Dose of SpiritFerm-activated carbon | | |
|--|------------------|-------------------------------------|-----------------|-----------------|
| | | 0.5 g | 1.0 g | 2.0 g |
| <i>Carbonyl compounds and acetals</i> | | | | |
| Acetaldehyde | 8.93 ± 0.25a | 8.49 ± 0.65ab | 7.78 ± 0.64bc | 7.45 ± 0.21c |
| Valeraldehyde | 0.23 ± 0.02b | 0.14 ± 0.02a | 0.12 ± 0.01a | 0.13 ± 0.01a |
| Hexanal | 2.19 ± 0.07b | 1.56 ± 0.16a | 1.41 ± 0.05a | 1.43 ± 0.08a |
| Furfural | 5.13 ± 0.38c | 4.10 ± 0.24b | 2.58 ± 0.13a | 2.37 ± 0.32a |
| Heptanal | 1.29 ± 0.06b | 0.92 ± 0.04a | 1.20 ± 0.08ab | 1.25 ± 0.11ab |
| Benzaldehyde | 0.83 ± 0.01c | 0.51 ± 0.02b | 0.35 ± 0.02a | 0.32 ± 0.04a |
| 3-Ethyl-4-heptanone | 0.17 ± 0.01b | 0.11 ± 0.00ab | 0.11 ± 0.01ab | 0.10 ± 0.01a |
| 2,3-Heptanedione | 0.40 ± 0.02c | 0.23 ± 0.01b | 0.20 ± 0.02b | 0.15 ± 0.01a |
| Acetaldehyde diethyl acetal | 27.74 ± 0.53b | 25.96 ± 1.46ab | 25.70 ± 1.08ab | 25.01 ± 1.49a |
| Isobutyraldehyde diethyl acetal | 1.24 ± 0.04b | 1.18 ± 0.05b | 1.12 ± 0.16b | 0.95 ± 0.08a |
| Isovaleraldehyde diethyl acetal | 4.25 ± 0.12b | 3.44 ± 0.22a | 3.11 ± 0.03a | 3.38 ± 0.17a |
| Diacetyl | 0.00 ± 0.00 | 1.21 ± 0.15a | 1.16 ± 0.11a | 0.97 ± 0.09b |
| <i>Alcohols</i> | | | | |
| Methanol | 121.09 ± 0.55c | 114.34 ± 3.09ab | 116.59 ± 3.24bc | 110.56 ± 2.11a |
| 1-Propanol | 466.03 ± 3.57c | 436.69 ± 7.42b | 390.20 ± 7.88a | 383.30 ± 6.49a |
| 2-Methyl-1-propanol | 2609.43 ± 10.46c | 2471.79 ± 5.39b | 1907.16 ± 7.50a | 1915.98 ± 3.45a |
| 1-Butanol | 10.44 ± 0.56a | 10.40 ± 1.27a | 10.49 ± 0.97a | 10.37 ± 0.88a |
| 3-Methyl-1-butanol | 694.12 ± 5.57c | 641.05 ± 6.93b | 476.55 ± 5.26a | 484.97 ± 11.51a |
| 2-Methyl-1-butanol | 296.51 ± 1.85c | 268.94 ± 4.17b | 204.67 ± 2.51a | 205.04 ± 4.25a |
| <i>Esters</i> | | | | |
| Ethyl acetate | 36.21 ± 0.51b | 36.08 ± 2.07b | 25.54 ± 0.54a | 25.15 ± 1.14a |
| Ethyl propanoate | 0.20 ± 0.02b | 0.13 ± 0.01a | 0.13 ± 0.02a | 0.12 ± 0.02a |
| Ethyl isobutyrate | 0.55 ± 0.09b | 0.36 ± 0.01a | 0.32 ± 0.01a | 0.30 ± 0.03a |
| Isobutyl acetate | 1.02 ± 0.58a | 1.06 ± 0.09a | 1.09 ± 0.07a | 0.88 ± 0.10a |
| Ethyl butyrate | 1.46 ± 0.09b | 0.92 ± 0.06a | 0.82 ± 0.03a | 0.80 ± 0.07a |
| Ethyl 2-methylbutanoate | 0.37 ± 0.02b | 0.24 ± 0.02a | 0.27 ± 0.01a | 0.22 ± 0.02a |
| Ethyl isovalerate | 0.46 ± 0.02b | 0.28 ± 0.01a | 0.28 ± 0.01a | 0.21 ± 0.02a |
| Isoamyl acetate | 28.08 ± 1.02c | 19.84 ± 0.89b | 16.98 ± 0.50a | 16.45 ± 0.79a |
| 2-Methylbutyl acetate | 8.74 ± 0.22b | 6.37 ± 0.07a | 6.56 ± 0.10a | 6.37 ± 0.07a |
| Ethyl valerate | 0.46 ± 0.03c | 0.31 ± 0.01b | 0.26 ± 0.01a | 0.26 ± 0.02a |
| Di-n-propyl succinate | 0.75 ± 0.01b | 0.53 ± 0.02a | 0.47 ± 0.02a | 0.52 ± 0.03a |
| Di-n-butyl succinate | 0.15 ± 0.01b | 0.11 ± 0.00a | 0.13 ± 0.00ab | 0.13 ± 0.00ab |
| Amyl propanoate | 0.11 ± 0.00b | 0.07 ± 0.01a | 0.06 ± 0.01a | 0.06 ± 0.00a |
| Ethyl caproate | 36.85 ± 0.41c | 24.37 ± 0.90b | 8.09 ± 0.14a | 7.98 ± 0.55a |
| Ethyl 3-hexenoate | 0.16 ± 0.01b | 0.05 ± 0.01a | 0.06 ± 0.01a | 0.05 ± 0.00a |
| Methyl hydrogen succinate | 2.09 ± 0.03b | 1.44 ± 0.10a | 1.32 ± 0.02a | 1.34 ± 0.09a |
| Amyl isobutyrate | 1.78 ± 0.07b | 1.07 ± 0.04a | 0.96 ± 0.01a | 0.89 ± 0.06a |
| Isoamyl butyrate | 0.26 ± 0.01b | 0.18 ± 0.01a | 0.17 ± 0.01a | 0.20 ± 0.01a |
| Ethyl enanthate | 5.52 ± 0.19b | 2.54 ± 0.10a | 2.03 ± 0.04a | 2.16 ± 0.10a |
| 3-Methylbutyl 2-methylbutyrate | 1.61 ± 0.03b | 0.98 ± 0.01a | 0.98 ± 0.01a | 0.97 ± 0.01a |
| 3-Methylbutyl isovalerate | 1.13 ± 0.01b | 0.51 ± 0.02a | 0.52 ± 0.01a | 0.47 ± 0.03a |
| Isobutyl caproate | 0.26 ± 0.02c | 0.17 ± 0.01b | 0.13 ± 0.01a | 0.13 ± 0.00a |
| Ethyl caprylate | 5.18 ± 0.23b | 2.75 ± 0.17a | 2.51 ± 0.09a | 2.61 ± 0.12a |
| Ethyl 2-methyloctanoate | 0.34 ± 0.01b | 0.30 ± 0.01b | 0.25 ± 0.02a | 0.22 ± 0.01a |
| Isoamyl caproate | 0.29 ± 0.01b | 0.12 ± 0.00a | 0.12 ± 0.01a | 0.13 ± 0.01a |
| Ethyl caprate | 1.74 ± 0.08c | 0.94 ± 0.03b | 0.27 ± 0.01a | 0.24 ± 0.01a |
| Ethyl laurate | 1.27 ± 0.00d | 0.74 ± 0.01c | 0.08 ± 0.01b | 0.04 ± 0.01a |
| 2-Methyl-nonyl propanoate | 0.13 ± 0.01b | 0.13 ± 0.01b | 0.07 ± 0.01a | 0.07 ± 0.00a |
| Ethyl palmitate | 0.02 ± 0.01a | 0.01 ± 0.00a | n.d. | n.d. |
| <i>Other compounds</i> | | | | |
| 2-Pentylfuran | 2.39 ± 0.03c | 0.44 ± 0.03b | 0.12 ± 0.01a | 0.13 ± 0.02a |
| Tetrahydro-4-methyl-2-(2-methyl-1-propenyl)-2H-pyran | 0.33 ± 0.02b | 0.15 ± 0.00a | 0.15 ± 0.01a | 0.13 ± 0.01a |
| 3-Phenylfuran | 0.04 ± 0.00b | 0.02 ± 0.00a | 0.02 ± 0.00a | 0.02 ± 0.00a |
| 1,5,7-Trimethyl-1,2,3,4-tetrahydronaphthalene | 3.74 ± 0.10d | 0.55 ± 0.03c | 0.36 ± 0.01b | 0.25 ± 0.01a |
| 1,1,5-Trimethyl-1,2-dihydronaphthalene | 0.48 ± 0.01b | 0.21 ± 0.01a | 0.23 ± 0.01a | 0.20 ± 0.00a |
| Tridecane | 0.84 ± 0.02c | 0.13 ± 0.01b | 0.07 ± 0.00a | 0.07 ± 0.01a |
| Dodecane | 0.09 ± 0.00b | 0.00 ± 0.00a | 0.00 ± 0.00a | 0.00 ± 0.00a |
| Styrene | 37.90 ± 0.60c | 18.31 ± 1.04b | 14.57 ± 0.33a | 19.13 ± 0.13b |

Note: n.d., Not detected; mean values in lines with different letters are significantly different ($p < 0.05$).

Aldehydes are volatile compounds known to have a negative influence on the quality of spirits. Acetaldehyde is considered by the IARC to be 'possibly carcinogenic to humans' (group 2B) (IARC

1999). Aldehydes with molecules with more than two carbon atoms, and in particular those with five or more (i.e., valeraldehyde and isovaleraldehyde, hexanal), are especially undesirable in agricultural

distillates, because even at low concentrations they may deteriorate the quality of spirits (Pielech-Przybylska et al. 2016).

Of the aldehydes in the tested agricultural distillate, acetaldehyde occurred in the largest quantity ($8.93 \pm 0.25 \text{ mg l}^{-1}$ alcohol 100% v/v). With an AC dose of 0.5 g per 100 ml of distillate, acetaldehyde content was only 5% lower than the control sample, at $8.49 \pm 0.65 \text{ mg l}^{-1}$ alcohol 100% v/v. Increasing the dose of adsorbent to 1 g per 100 ml of distillate led to larger ($p < 0.05$) reductions in the concentration of this compound, to $7.78 \pm 0.64 \text{ mg l}^{-1}$ alcohol 100% v/v. However, further increasing the dose of adsorbent to 2 g per 100 ml of distillate did not result in significant further decreases in acetaldehyde content. The low adsorption capacity of acetaldehyde on the AC surface is associated with its relatively high vapour pressure (Yao 2008).

Analogous tendencies were observed in the case of furfural and benzaldehyde. However, it should be noted that the concentrations of these two compounds were reduced by approximately 50–58% in the sample treated with 1 g of AC per 100 ml of distillate in comparison with the control, whereas acetaldehyde was reduced by only approximately 13%. Mattson et al. (1969) report the formation, in compounds containing an aromatic ring such as benzaldehyde, of donor–acceptor complexes between the aromatic ring and the surface of the adsorbent. Moreover, the presence of a carboxy group (electron withdrawing groups) on the aromatic ring may lower the electronic density of the molecules, making it easier for the aromatic ring to act as an acceptor. These facts may explain the higher absorbance of furfural and benzaldehyde.

At a dose of 0.5 g per 100 ml of distillate, treatment with SpiritFerm-AC also caused concentrations of valeraldehyde to decrease by approximately 43.5% and concentrations of hexanal to reduce by about 34% in relation to the control sample. However, increasing the dose of adsorbent did not cause significant further decreases in the content of these compounds ($p > 0.05$).

Other ubiquitous compounds in alcoholic beverages include acetals, which form rapidly in distillates. The most abundant compound in this group is acetaldehyde diethyl acetal (1,1-

diethoxyethane), which is found in high concentrations in whiskies, especially malt whisky (Nykänen & Nykänen 1991). In our study, with adsorbent doses of $0.5 \text{ g } 100 \text{ ml}^{-1}$ and above, the concentrations of acetals reduced slightly (by only up to 10% for acetaldehyde diethyl acetal, by up to approximately 23% for isobutyraldehyde diethyl acetal and by up to about 27% for isovaleraldehyde diethyl acetal). We also measured the concentration of diacetyl in samples treated with different doses of SpiritFerm preparation. However, changes in the concentration of diacetyl did not show any correlation with the dose of adsorbent.

The compound that may be detrimental to human health is methanol. Its release involves a specific pectolytic enzyme, pectin methylesterase (Adam & Versini 1996). Due to its toxicity, European Union Regulation No. 110/2008 sets tight limits on the acceptable concentrations of methanol in ethyl alcohols of agricultural origin (i.e., rectified spirit), wine spirits and fruit spirits. A certain quantity of this compound is by necessity present in natural brandies due to their fruit origin (Nikićević & Tešević 2005). There are currently no legal limits placed on the content of methanol in distillates of agricultural origin (European Commission 2008). This may be associated with the low pectin content in the starchy raw materials used in distilleries.

Similar low levels of adsorption were observed for methanol (up to 10% in relation to the control) during treatment with SpiritFerm-AC, irrespective of the dose of AC (Table 2). Oliveira et al. (2010), who investigated the adsorption of methanol in AC, observed that methanol adsorption could be improved by using impregnated AC – such as with LiCl (13.7% wt). In their study, this sorbent showed 56% higher adsorption of methanol than untreated AC.

From a quantitative point of view, the most important group of fermentation byproducts is constituted by higher alcohols, also known as fusel oils, represented mainly by *n*-propanol, amyl alcohol and its isomers, i.e., 2-methyl-1-butanol and 3-methyl-1-butanol. These compounds play an important role in determining the flavour qualities of spirits, such as whisky (Lyons 2003) and vodka (Balcerek, Pielech-Przybylska, Dziekońska-Kubczak et al. 2016).

With regard to changes in the concentration of higher alcohols, the optimal dose of AC was found

to be 1 g per 100 ml of distillate. Treatment of samples with 2 g of AC per 100 ml of distillate did not result in significant further reductions in the levels of higher alcohols ($p > 0.05$).

Esters are an important group of volatile fermentation byproducts in terms of the spirits' aroma (Nykänen & Suomalainen 1983). Of the esters detected in the tested agricultural distillate, ethyl acetate and isoamyl acetate were present in the highest concentrations (36.21 ± 0.51 and 28.08 ± 1.02 mg l⁻¹ alcohol 100% v/v, respectively). The smallest reduction in the concentrations of these compounds was noted in the sample treated with 0.5 g of SpiritFerm preparation per 100 ml of distillate. Increasing the dose of adsorbent to 1 g per 100 ml of distillate resulted in statistically significant improvements in the reduction of these esters, as well as of ethyl caproate, ethyl laurate and 2-methyl-nonyl propanoate. However, increasing the adsorbent dose to 2 g 100 ml⁻¹ distillate did not result in further reductions in these congeners. The amounts of other esters identified in the distillate, listed in Table 2, did not vary significantly ($p > 0.05$), independent of the dose of adsorbent.

Potential markers for the botanical origin of raw spirits produced from maize, rye, triticale and wheat include 2-pentylfuran, 3-phenylfuran and styrene (Biernacka & Wardencki 2012). These compounds have also been detected in cereal malts (Briggs 1998). Furan and its derivatives originate from many sources, and are formed in multiple processes, including thermal degradation of reducing sugars, thermal degradation of certain amino acids or Maillard reactions between reducing sugars and amino acids (Yaylayan 2006). Furan has been classified as 'possibly carcinogenic to humans' (group 2B) by the IARC (1995). Styrene (a benzene derivative) is formed by the thermal decarboxylation of cinnamic acid during beer wort boiling or by enzymatic decarboxylation during alcoholic fermentation (Schwarz et al. 2012) and has also been included in group 2B by the IARC (2002), on the basis of limited evidence of its carcinogenicity in animal tests, supported by an extensive set of other relevant data, including biomarkers of exposure and effect.

The concentrations of 2-pentylfuran and 3-phenylfuran in the tested agricultural distillate were

2.39 ± 0.03 and 0.04 ± 0.00 mg l⁻¹ alcohol 100% v/v, respectively. 2-Pentylfuran was reduced by approximately 82% (in relation to the control) with an adsorbent dose of 0.5 g per 100 ml of distillate. Doses of 1 and 2 g per 100 ml of distillate gave similar results ($p > 0.05$), with reductions in 2-pentylfuran of approximately 95%, while the concentration of 3-phenylfuran reduced by about 50%, regardless of the dose of AC. The concentrations of tetrahydro-4-methyl-2-(2-methyl-1-propenyl)-2H-pyran, 1,1,5-trimethyl-1,2-dihydronaphthalene and styrene were not correlated with the dose of adsorbent, and were also reduced by up to approximately 50% compared with the control.

When assessing the changes in concentrations of alkanes, i.e., dodecane and tridecane, already the dose of 0.5 g AC per 100 ml distillate was sufficient for their efficient removing; dodecane was removed completely, whereas tridecane content was lowered by 84.5% in relation to the control (Table 2).

The results of Zhang et al. (2000) who studied adsorption capacity of AC for *n*-alkanes (C5–C11) showed that the *n*-alkanes' mass adsorbed increased with the amount of carbon in the molecules. The rate of increase appeared to slow down when the molecular size as represented by the radius of gyration exceeded 5 Å. Generally, the adsorbed mass on AC was proportional to the size of these molecules.

The contact time of agricultural distillate with SpiritFerm-AC in the above-mentioned set of samples was 1 h. In the supporting experiments, the effectiveness of adsorption of volatiles in the shorter (0.5 h) and the longer (2 h) contact times were assessed. The obtained results revealed that the contact time 0.5 h proved to be insufficient for effective purification of the tested distillate. The samples in contact with AC for 1 h showed the largest reductions in the concentrations of most volatile compounds. Increasing the contact time to 2 h did not lead to significant further reductions ($p > 0.05$) in the concentration of the determined compounds (data not shown). These results are in agreement with those of Siříštová et al. (2012), who showed that using higher flow rates during the filtration process does not reduce the adsorption efficiency of AC for congeners. This suggests that the duration of this part of the production process can be kept to a minimum.

Effect of ethanol concentration

An important issue for producers of spirit beverages is finding the optimal concentration of ethanol (i.e., alcohol strength by volume) to ensure maximal removal of volatile impurities and the optimal organoleptic characteristics. The results of our investigation into the effects of ethanol content on the reduction of volatile fermentation byproducts in samples of agricultural distillate treated with SpiritFerm-AC are presented in Table 3.

The intensity of acetaldehyde adsorption showed an inverse relation to the ethanol concentration. The content of acetaldehyde reached lowest values (5.71 ± 0.54 to 5.90 ± 0.72 mg l⁻¹ alcohol 100% v/v) in solutions with an ethanol content of 70–80% v/v, while in solutions with an ASV of 40% v/v there was no statistically significant decrease in relation to the control sample (8.67 ± 0.27 mg l⁻¹ alcohol 100% v/v). Concentrations of other carbonyl compounds did not follow the same pattern. For example, valeraldehyde concentrations did not differ statistically ($p > 0.05$) in any of the tested samples with ethanol contents of between 40% and 80% v/v. Hexanal, furfural, heptanal, benzaldehyde and 2,3-heptanedione showed the opposite tendency to that observed for acetaldehyde, decreasing in concentration as the ethanol content in the tested samples was lowered. The concentration of acetals did not decrease significantly after treatment with AC, regardless of the concentration of ethanol ($p > 0.05$). Interestingly, diacetyl was detected in the samples treated with AC-based adsorbent, but was not detected in the control sample (distillate before treatment).

As with the changes in the content of acetaldehyde, the largest decrease in methanol content was observed in the sample with an ASV of 80%, while the smallest reduction was seen in the sample with an ethanol content of 40% v/v ($p < 0.05$). This was probably due to the association phenomenon, whereby hydrogen bonds are formed between water molecules and, for example, alcohols. As a consequence, the molecular weight of compounds (such as methanol) increases and their volatility decreases, enabling higher adsorption on the surface of AC (Balcerek, Pielech-Przybylska, Patelski et al. 2016). However,

it should be noted that all the tested samples of agricultural distillate (i.e., raw spirit), including the control sample, met the requirements of European Union Regulation No. 110/2008 (European Commission 2008) for the limit concentration of methanol in ethyl alcohol of agricultural origin (i.e., rectified spirit), which should amount to no more than 30 g hl⁻¹ alcohol 100% v/v (i.e., 300 mg l⁻¹).

In our study, the largest decrease in the concentration of higher alcohols (approximately 30% in relation to the control) ($p < 0.05$) after treatment with AC was observed in samples of agricultural distillate with an alcohol content of 40% v/v. Increasing the ASV resulted in smaller reductions in the levels of these compounds. Higher alcohols show limited solubility at lower ethanol concentrations (Clarke & Bakker 2004), and this probably explains their higher adsorption in samples with low alcohol content.

With regard to esters, the levels of ethyl acetate were highest in samples with ethanol content of 80% v/v, and showed a tendency to decrease in samples with lower ethanol contents ($p < 0.05$). However, the lowest concentration of ethyl acetate was observed in a solution with ethanol content of 40% v/v. The concentration of ethyl acetate in this sample was only by around 33% lower than in the control.

Apart from ethyl acetate, relatively low concentrations of esters formed during the reaction of acetic acid and higher alcohols, as well as esters of fatty acids C6–C10 and ethanol (i.e., ethyl caproate (hexanoate), ethyl caprylate (octanoate), ethyl enanthate (heptanoate), isoamyl caproate, ethyl caprate (decanoate)) were also present (Table 1). These esters have limited solubility in water (Matias-Guiu et al. 2016), which probably explains their higher adsorption in solutions with lower ethanol contents, compared with samples with higher ASV ($p < 0.05$). As shown in Table 1, the decreases in the concentrations of the majority of esters were larger when the ASV of the tested solutions was lowered.

The highest adsorption of derivatives of furan (approximately 98% for 2-pentylfuran and 75% for 3-phenylfuran, respectively) ($p < 0.05$), and consequently their lowest concentrations in the treated samples, occurred in distillate diluted to an ASV

Table 3. Effect of ethanol concentration in samples of agricultural distillate on the adsorption of volatile compounds by SpiritFerm-activated carbon (1.0 g 100 ml⁻¹; contact time of 1 h).

| Compound (mg l ⁻¹ alcohol 100% v/v) | Ethanol concentration | | | | | |
|--|-----------------------|------------------|-----------------|-----------------|------------------|------------------|
| | Control sample | 40% v/v | 50% v/v | 60% v/v | 70% v/v | 80% v/v |
| <i>Carbonyl compounds and acetals</i> | | | | | | |
| Acetaldehyde | 8.93 ± 0.25a | 8.67 ± 0.27a | 7.64 ± 0.44b | 7.11 ± 0.33b | 5.71 ± 0.54c | 5.90 ± 0.72c |
| Valeraldehyde | 0.23 ± 0.02b | 0.13 ± 0.01a | 0.12 ± 0.01a | 0.16 ± 0.03a | 0.15 ± 0.01a | 0.16 ± 0.01a |
| Hexanal | 2.19 ± 0.07c | 1.41 ± 0.05a | 1.41 ± 0.05a | 1.51 ± 0.06a | 1.72 ± 0.07b | 1.72 ± 0.09b |
| Furfural | 5.13 ± 0.38e | 1.63 ± 0.07b | 2.58 ± 0.13c | 3.32 ± 0.12a | 3.49 ± 0.03a | 3.86 ± 0.11d |
| Heptanal | 1.29 ± 0.06c | 0.86 ± 0.08b | 1.20 ± 0.08a | 1.28 ± 0.08a | 0.97 ± 0.08b | 1.22 ± 0.02a |
| Benzaldehyde | 0.83 ± 0.01e | 0.51 ± 0.01b | 0.65 ± 0.02c | 0.70 ± 0.01d | 0.76 ± 0.01a | 0.73 ± 0.02a |
| 3-Ethyl-4-heptanone | 0.17 ± 0.01b | 0.09 ± 0.01c | 0.11 ± 0.01a | 0.11 ± 0.00a | 0.14 ± 0.01d | 0.18 ± 0.01b |
| 2,3-Heptanedione | 0.40 ± 0.02e | 0.20 ± 0.01a | 0.20 ± 0.02a | 0.27 ± 0.02b | 0.32 ± 0.01c | 0.37 ± 0.01d |
| Acetaldehyde diethyl acetal | 27.74 ± 0.53a | 27.20 ± 0.42a | 25.97 ± 1.72ab | 27.20 ± 0.82a | 24.83 ± 1.22b | 27.04 ± 1.24a |
| Isobutyraldehyde diethyl acetal | 1.24 ± 0.04bc | 1.15 ± 0.06b | 1.42 ± 0.16ac | 1.50 ± 0.12a | 1.62 ± 0.09ad | 1.81 ± 0.16d |
| Isovaleraldehyde diethyl acetal | 4.25 ± 0.12a | 3.03 ± 0.08a | 3.11 ± 0.03a | 3.42 ± 0.14b | 3.63 ± 0.03c | 3.96 ± 0.08d |
| Diacetyl | n.d. | 1.72 ± 0.12b | 1.13 ± 0.13c | 1.49 ± 0.15a | 1.38 ± 0.12a | 1.62 ± 0.21ab |
| <i>Alcohols</i> | | | | | | |
| Methanol | 121.09 ± 0.55b | 116.43 ± 4.6ab | 116.56 ± 4.00ab | 114.13 ± 3.41a | 83.85 ± 3.59c | 86.65 ± 2.49c |
| 1-Propanol | 466.03 ± 3.57e | 339.55 ± 4.34b | 390.20 ± 7.88c | 443.81 ± 7.35a | 444.66 ± 5.34a | 456.18 ± 2.27d |
| 2-Methyl-1-propanol | 2609.43 ± 10.46e | 1922.06 ± 29.28a | 1907.94 ± 4.25a | 2182.72 ± 6.71b | 2447.86 ± 13.65c | 2513.80 ± 10.11d |
| 1-Butanol | 10.44 ± 0.56b | 9.10 ± 0.62a | 9.21 ± 0.46a | 10.20 ± 0.57b | 10.31 ± 0.54b | 10.77 ± 0.68b |
| 3-Methyl-1-butanol | 694.12 ± 5.57b | 460.63 ± 3.95d | 476.57 ± 4.70c | 636.52 ± 0.82a | 635.71 ± 6.15a | 690.43 ± 1.88b |
| 2-Methyl-1-butanol | 296.51 ± 1.85f | 217.91 ± 2.19b | 204.67 ± 2.40a | 268.07 ± 6.32c | 275.39 ± 3.25d | 285.69 ± 2.82e |
| <i>Esters</i> | | | | | | |
| Ethyl acetate | 36.21 ± 0.51a | 24.37 ± 0.33d | 25.54 ± 0.54c | 27.11 ± 0.96c | 30.15 ± 0.65b | 32.35 ± 1.51b |
| Ethyl propanoate | 0.20 ± 0.02b | 0.14 ± 0.02a | 0.13 ± 0.02a | 0.14 ± 0.02a | 0.17 ± 0.01b | 0.19 ± 0.01b |
| Ethyl isobutyrate | 0.55 ± 0.09c | 0.27 ± 0.01a | 0.32 ± 0.01a | 0.41 ± 0.01b | 0.48 ± 0.01b | 0.58 ± 0.01c |
| Isobutyl acetate | 1.02 ± 0.58a | 0.83 ± 0.12a | 1.09 ± 0.07a | 1.25 ± 0.10b | 1.28 ± 0.13b | 1.28 ± 0.06b |
| Ethyl butyrate | 1.46 ± 0.09b | 0.76 ± 0.04a | 0.85 ± 0.01a | 1.02 ± 0.10c | 1.18 ± 0.06d | 1.38 ± 0.03b |
| Ethyl 2-methylbutanoate | 0.37 ± 0.02c | 0.23 ± 0.01d | 0.27 ± 0.01e | 0.31 ± 0.02a | 0.33 ± 0.02ab | 0.35 ± 0.00bc |
| Ethyl isovalerate | 0.46 ± 0.02b | 0.26 ± 0.01a | 0.28 ± 0.01a | 0.37 ± 0.01c | 0.39 ± 0.01d | 0.46 ± 0.02b |
| Isoamyl acetate | 28.08 ± 1.02e | 17.15 ± 0.31b | 18.98 ± 0.50c | 20.76 ± 0.36d | 25.93 ± 0.25a | 25.90 ± 0.43a |
| 2-Methylbutyl acetate | 8.74 ± 0.22f | 5.56 ± 0.23b | 6.56 ± 0.10a | 6.68 ± 0.10a | 7.13 ± 0.17c | 8.31 ± 0.18d |
| Ethyl valerate | 0.46 ± 0.03e | 0.23 ± 0.01a | 0.26 ± 0.01a | 0.26 ± 0.01a | 0.25 ± 0.01a | 0.46 ± 0.01c |
| Di-n-propyl succinate | 0.75 ± 0.01a | 0.43 ± 0.01b | 0.47 ± 0.02c | 0.56 ± 0.01a | 0.58 ± 0.01a | 0.67 ± 0.02d |
| Di-n-butyl succinate | 0.15 ± 0.01e | 0.12 ± 0.01a | 0.13 ± 0.00a | 0.16 ± 0.01a | 0.15 ± 0.01a | 0.28 ± 0.21a |
| Amyl propanoate | 0.11 ± 0.00e | 0.06 ± 0.01a | 0.06 ± 0.01a | 0.06 ± 0.00a | 0.09 ± 0.00b | 0.10 ± 0.00c |
| Ethyl caproate | 36.85 ± 0.41c | 5.73 ± 0.17a | 8.09 ± 0.14b | 21.97 ± 0.49c | 25.96 ± 0.44d | 31.01 ± 0.44e |
| Ethyl 3-hexenoate | 0.16 ± 0.01d | 0.06 ± 0.00a | 0.06 ± 0.01a | 0.05 ± 0.01a | 0.09 ± 0.00b | 0.09 ± 0.00b |
| Methyl hydrogen succinate | 2.09 ± 0.03f | 1.14 ± 0.02c | 1.32 ± 0.02a | 1.32 ± 0.02a | 1.58 ± 0.06b | 1.62 ± 0.01b |
| Amyl isobutyrate | 1.78 ± 0.07d | 0.83 ± 0.01a | 0.96 ± 0.01b | 1.19 ± 0.02c | 1.49 ± 0.02d | 1.59 ± 0.04e |
| Isoamyl butyrate | 0.26 ± 0.01e | 0.15 ± 0.01a | 0.17 ± 0.01b | 0.16 ± 0.00ab | 0.19 ± 0.00c | 0.20 ± 0.01c |
| Ethyl enanthate | 5.52 ± 0.19d | 1.63 ± 0.05b | 2.03 ± 0.04c | 3.61 ± 0.05a | 3.68 ± 0.06a | 4.44 ± 0.04d |
| 3-Methylbutyl 2-methylbutyrate | 1.61 ± 0.03e | 0.96 ± 0.01a | 0.98 ± 0.01a | 1.17 ± 0.09b | 1.23 ± 0.03b | 1.40 ± 0.02c |
| 3-Methylbutyl isovalerate | 1.13 ± 0.01d | 0.54 ± 0.01a | 0.52 ± 0.01a | 0.68 ± 0.01b | 0.78 ± 0.01c | 1.06 ± 0.06d |
| Isobutyl caproate | 0.26 ± 0.02e | 0.11 ± 0.01b | 0.13 ± 0.01a | 0.14 ± 0.00a | 0.17 ± 0.01c | 0.21 ± 0.01d |
| Ethyl caprylate | 51.82 ± 0.23d | 25.02 ± 0.38a | 25.13 ± 0.09a | 34.13 ± 0.42b | 39.31 ± 0.16c | 45.33 ± 0.59d |
| Ethyl 2-methyloctanoate | 0.34 ± 0.01e | 0.26 ± 0.01b | 0.25 ± 0.02b | 0.34 ± 0.02a | 0.33 ± 0.01a | 0.32 ± 0.01a |
| Isoamyl caproate | 0.29 ± 0.01f | 0.11 ± 0.00a | 0.12 ± 0.01a | 0.16 ± 0.01b | 0.23 ± 0.01c | 0.26 ± 0.01d |
| Ethyl caprate | 1.74 ± 0.08a | 0.30 ± 0.02a | 0.27 ± 0.01a | 0.24 ± 0.00a | 0.98 ± 0.03b | 1.51 ± 0.03c |
| Ethyl laurate | 1.27 ± 0.00d | 0.40 ± 0.03a | 0.38 ± 0.01a | 0.36 ± 0.01a | 0.43 ± 0.01b | 0.63 ± 0.02c |
| 2-Methyl-nonyl propanoate | 0.13 ± 0.01a | 0.05 ± 0.01a | 0.07 ± 0.01c | 0.04 ± 0.00a | 0.09 ± 0.00b | 0.10 ± 0.00b |
| Ethyl palmitate | 0.02 ± 0.01e | 0.02 ± 0.00a | n.d. | n.d. | 0.01 ± 0.00a | 0.01 ± 0.00a |
| <i>Other compounds</i> | | | | | | |
| 2-Pentylfuran | 2.39 ± 0.03f | 0.05 ± 0.01a | 0.12 ± 0.01a | 0.54 ± 0.05b | 0.91 ± 0.02c | 1.97 ± 0.08d |
| Tetrahydro-4-methyl-2-(2-methyl-1-propenyl)-2H-pyran | 0.33 ± 0.02e | 0.14 ± 0.01a | 0.15 ± 0.01a | 0.17 ± 0.01b | 0.18 ± 0.00b | 0.23 ± 0.01c |
| 3-Phenylfuran | 0.04 ± 0.00e | 0.01 ± 0.00a | 0.02 ± 0.00b | 0.03 ± 0.00c | 0.03 ± 0.00c | 0.03 ± 0.00c |
| 1,5,7-Trimethyl-1,2,3,4-tetrahydronaphthalene | 3.74 ± 0.10a | 0.19 ± 0.02a | 0.36 ± 0.01a | 1.47 ± 0.07b | 1.69 ± 0.03c | 3.16 ± 0.11d |
| 1,1,5-Trimethyl-1,2-dihydronaphthalene | 0.48 ± 0.01d | 0.04 ± 0.01c | 0.23 ± 0.01ab | 0.22 ± 0.01a | 0.25 ± 0.02b | 0.44 ± 0.01d |
| Tridecane | 0.84 ± 0.02c | 0.03 ± 0.00a | 0.07 ± 0.00b | 0.19 ± 0.01c | 0.63 ± 0.04d | 0.80 ± 0.01e |
| Dodecane | 0.09 ± 0.00e | n.d. | n.d. | 0.03 ± 0.00a | 0.07 ± 0.00b | 0.09 ± 0.01c |
| Styrene | 37.90 ± 0.60a | 9.02 ± 0.40a | 14.57 ± 0.33b | 18.22 ± 0.88c | 26.96 ± 1.55d | 31.71 ± 1.18e |

Note: n.d., Not detected; mean values in lines with different letters are significantly different ($p < 0.05$).

of 40% v/v. On the other hand, increasing the alcohol concentration in the agricultural distillate solutions lowered the ability of SpiritFerm-AC to adsorb 2-pentylfuran and 3-phenylfuran. Analogous tendencies were observed in the case of tetrahydro-4-methyl-2-(2-methyl-1-propenyl)-2H-pyran, naphthalene derivatives, hydrocarbons (dodecane, tridecane) and styrene.

Comparison of adsorbents

Two other adsorbents, Spiricol preparation (a granular adsorbent based on AC and silicon dioxide) and DistiPur preparation (a mineral adsorbent based on silicon dioxide), were tested as comparisons for SpiritFerm-AC. The results are presented in Table 4. The lowest content of acetaldehyde was determined in the sample treated with Spiricol preparation ($p < 0.05$), while the highest concentration of this compound was assayed in the sample treated with DistiPur preparation. The concentrations of aldehydes, such as valeraldehyde, and furfural were similar in samples treated with SpiritFerm and Spiricol ($p > 0.05$). Treatment with Spiricol resulted in the lowest concentrations of acetaldehyde diethyl acetal and isobutyraldehyde diethyl acetal.

The methanol concentration in the distillate reduced by similar amounts ($p > 0.05$) in all the tested samples, independently of the adsorbent type. On the other hand, the largest decrease ($p < 0.05$) in the higher alcohols content was observed in the sample treated with SpiritFerm preparation. DistiPur and Spiricol showed similar ($p > 0.05$) adsorption efficiency for higher alcohols.

In the majority of samples, treatment with mineral adsorbent based on silicon dioxide (DistiPur) did not lead to reduced concentrations of esters, including ethyl acetate (which occurred in the highest concentration). The lowest concentrations of ethyl acetate, as well as of esters of higher carboxylic acids and ethanol (ethyl isobutyrate, ethyl 2-methylbutanoate, ethyl caproate, ethyl 3-hexenoate, ethyl caprate and ethyl laurate), were noted in samples treated with SpiritFerm-AC. Spiricol was the most effective adsorbent of furan and naphthalene derivatives, as well as of styrene.

Sensory evaluation

Each set of samples was evaluated separately for changes in its organoleptic characteristics, including colour, clearness, odour and taste (Figure 1). All the tested samples in each set of experiments were colourless and clear. Importantly, for assessing the effect of the amount of AC used for the treatment of agricultural distillate on its organoleptics, the highest score was given to the sample treated with 1 g of AC per 100 ml of distillate. This sample was characterised by a delicate and pleasant aroma and taste. Moreover, all samples treated with 1 g of SpiritFerm-AC per 100 ml of distillate, independently of its initial ASV, received similar scores ($p > 0.05$), higher than that of the control sample ($p < 0.05$).

The differences in the chemical compositions of samples treated with AC and silica (Spiricol preparation) or exclusively with silica (DistiPur preparation) resulted in statistically significant differences ($p < 0.05$) in their sensory assessments.

The most highly rated distillate was the sample treated with Spiricol preparation. This result may be due to the fact that this sample contained the lowest concentrations of aldehydes, including acetaldehyde and isovaleraldehyde (Table 4). The sample of agricultural distillate after treatment with AC was also described as having a pleasant aroma and delicate flavour, despite receiving a lower score. No noticeable improvement was reported in the sample treated with DistiPur preparation, probably because of the low degree of purification.

Conclusions

The results of this study indicate that treatment with appropriate adsorbents may improve the chemical composition and organoleptic quality of agricultural distillates. Parameters such as the dose of adsorbent (surface area) and the concentration of ethanol in the distillate, influence the effectiveness with which volatile congeners can be removed.

An interesting adsorbent for the elimination of impurities from agricultural distillate was revealed to be a preparation consisting of AC and silica (Spiricol). The agricultural distillate treated with this adsorbent was assessed most highly in terms of aroma and taste. Combining AC with other adsorbents may therefore be an effective method to reduce

Table 4. Effect of adsorbent type on the concentration of volatile compounds in agricultural distillate samples (dose of each adsorbent is 1.0 g 100 ml⁻¹; ethanol concentration 50% v/v; contact time of 1 h).

| Compound (mg l ⁻¹ alcohol 100% v/v) | Control sample | Adsorbent | | |
|--|------------------|-----------------|------------------|------------------|
| | | SpiritFerm | DistiPur | Spiricol |
| <i>Carbonyl compounds and acetals</i> | | | | |
| Acetaldehyde | 8.93 ± 0.25b | 7.80 ± 0.84a | 8.42 ± 0.24ab | 5.98 ± 0.21c |
| Valeraldehyde | 0.23 ± 0.02b | 0.12 ± 0.01a | n.d. | 0.09 ± 0.02a |
| Hexanal | 2.19 ± 0.07d | 1.41 ± 0.05b | 1.78 ± 0.04c | 1.09 ± 0.09a |
| Furfural | 5.13 ± 0.38b | 2.58 ± 0.13a | 4.06 ± 0.24b | 2.27 ± 0.17a |
| Heptanal | 1.29 ± 0.06a | 1.20 ± 0.08a | 1.25 ± 0.10a | 0.52 ± 0.04b |
| Benzaldehyde | 0.83 ± 0.01c | 0.65 ± 0.02b | 1.06 ± 0.08d | 0.16 ± 0.02a |
| 3-Ethyl-4-heptanone | 0.17 ± 0.01b | 0.11 ± 0.01ab | 0.14 ± 0.01b | 0.09 ± 0.02a |
| 2,3-Heptanedione | 0.40 ± 0.02c | 0.20 ± 0.02b | 0.20 ± 0.02b | 0.15 ± 0.01a |
| Acetaldehyde diethyl acetal | 27.74 ± 0.53a | 26.53 ± 1.78a | 27.15 ± 2.43a | 27.38 ± 2.80a |
| Isobutyraldehyde diethyl acetal | 1.24 ± 0.04b | 1.42 ± 0.16c | 1.24 ± 0.09b | 0.88 ± 0.13a |
| Isovaleraldehyde diethyl acetal | 4.25 ± 0.12a | 3.11 ± 0.03c | 4.17 ± 0.14a | 1.88 ± 0.08b |
| Diacetyl | n.d. | 1.18 ± 0.17a | 1.17 ± 0.13a | n.d. |
| <i>Alcohols</i> | | | | |
| Methanol | 121.09 ± 0.55b | 116.40 ± 3.78a | 114.40 ± 3.08a | 113.12 ± 4.86a |
| 1-Propanol | 466.03 ± 3.57c | 390.20 ± 7.88a | 436.85 ± 7.98b | 451.74 ± 14.68bc |
| 2-Methyl-1-propanol | 2609.43 ± 10.46c | 1907.94 ± 4.25a | 2523.57 ± 11.03b | 2514.86 ± 9.74b |
| 1-Butanol | 10.44 ± 0.56a | 9.21 ± 0.46a | 10.83 ± 1.15a | 10.27 ± 1.04a |
| 3-Methyl-1-butanol | 694.12 ± 5.57c | 476.57 ± 4.70a | 677.33 ± 17.85b | 653.27 ± 14.32b |
| 2-Methyl-1-butanol | 296.51 ± 1.85b | 204.67 ± 2.40a | 284.09 ± 17.44b | 274.07 ± 17.31b |
| <i>Esters</i> | | | | |
| Ethyl acetate | 36.21 ± 0.51c | 25.54 ± 0.54a | 36.99 ± 3.07c | 32.35 ± 1.89b |
| Ethyl propanoate | 0.20 ± 0.02c | 0.13 ± 0.02a | 0.18 ± 0.01bc | 0.15 ± 0.02ab |
| Ethyl isobutyrate | 0.55 ± 0.09b | 0.32 ± 0.01a | 0.55 ± 0.08b | 0.49 ± 0.02b |
| Isobutyl acetate | 1.02 ± 0.58a | 1.09 ± 0.07a | 1.22 ± 0.08a | 1.02 ± 0.06a |
| Ethyl butyrate | 1.46 ± 0.09c | 0.85 ± 0.01a | 1.29 ± 0.07b | 1.00 ± 0.04a |
| Ethyl 2-methylbutanoate | 0.37 ± 0.02b | 0.27 ± 0.01a | 0.33 ± 0.01ab | 0.33 ± 0.01ab |
| Ethyl isovalerate | 0.46 ± 0.02c | 0.28 ± 0.01a | 0.43 ± 0.01c | 0.35 ± 0.01b |
| Isoamyl acetate | 28.08 ± 1.02b | 18.98 ± 0.50a | 27.12 ± 0.60b | 18.83 ± 0.52a |
| 2-Methylbutyl acetate | 8.74 ± 0.22c | 6.56 ± 0.10b | 8.34 ± 0.21c | 5.17 ± 0.18a |
| Ethyl valerate | 0.46 ± 0.03b | 0.26 ± 0.01a | 0.44 ± 0.01b | 0.24 ± 0.01a |
| Di-n-propyl succinate | 0.75 ± 0.01c | 0.47 ± 0.02b | 0.70 ± 0.01c | 0.12 ± 0.01a |
| Di-n-butyl succinate | 0.15 ± 0.01a | 0.13 ± 0.00a | 0.12 ± 0.00a | 0.13 ± 0.00a |
| Amyl propanoate | 0.11 ± 0.00b | 0.06 ± 0.01a | 0.11 ± 0.01b | 0.06 ± 0.00a |
| Ethyl caproate | 36.85 ± 0.41d | 8.09 ± 0.14a | 31.07 ± 0.63c | 18.33 ± 0.61b |
| Ethyl 3-hexenoate | 0.16 ± 0.01c | 0.06 ± 0.01a | 0.15 ± 0.01c | 0.11 ± 0.01b |
| Methyl hydrogen succinate | 2.09 ± 0.03d | 1.32 ± 0.02b | 1.70 ± 0.08c | 0.32 ± 0.03a |
| Amyl isobutyrate | 1.78 ± 0.07b | 0.96 ± 0.01a | 1.69 ± 0.04b | 0.93 ± 0.02a |
| Isoamyl butyrate | 0.26 ± 0.01c | 0.17 ± 0.01b | 0.22 ± 0.01c | 0.12 ± 0.01a |
| Ethyl enanthate | 5.52 ± 0.19c | 2.03 ± 0.04b | 5.41 ± 0.18c | 1.48 ± 0.13a |
| 3-Methylbutyl 2-methylbutyrate | 1.61 ± 0.03c | 0.98 ± 0.01b | 1.52 ± 0.09c | 0.63 ± 0.02a |
| 3-Methylbutyl isovalerate | 1.13 ± 0.01c | 0.52 ± 0.01b | 1.10 ± 0.04c | 0.38 ± 0.03a |
| Isobutyl caproate | 0.26 ± 0.02c | 0.13 ± 0.01b | 0.27 ± 0.01c | 0.03 ± 0.01a |
| Ethyl caprylate | 51.82 ± 0.23d | 25.13 ± 0.09b | 50.39 ± 0.91c | 9.78 ± 0.41a |
| Ethyl 2-methyloctanoate | 0.34 ± 0.01c | 0.25 ± 0.02a | 0.28 ± 0.01b | 0.22 ± 0.01a |
| Isoamyl caproate | 0.29 ± 0.01c | 0.12 ± 0.01b | 0.36 ± 0.01d | 0.04 ± 0.00a |
| Ethyl caprate | 1.74 ± 0.08c | 0.27 ± 0.01a | 1.10 ± 0.17b | 1.25 ± 0.13b |
| Ethyl laurate | 1.27 ± 0.00d | 0.08 ± 0.01a | 0.98 ± 0.10b | 1.12 ± 0.00c |
| 2-Methyl-nonyl propanoate | 0.13 ± 0.01b | 0.07 ± 0.01a | 0.12 ± 0.00b | 0.06 ± 0.01a |
| Ethyl palmitate | 0.02 ± 0.01a | n.d. | 0.01 ± 0.00a | n.d. |
| <i>Other compounds</i> | | | | |
| 2-Pentylfuran | 2.39 ± 0.03d | 0.12 ± 0.01b | 2.00 ± 0.14c | 0.05 ± 0.02a |
| Tetrahydro-4-methyl-2-(2-methyl-1-propenyl)-2H-pyran | 0.33 ± 0.02c | 0.15 ± 0.01b | 0.24 ± 0.01c | 0.07 ± 0.01a |
| 3-Phenylfuran | 0.04 ± 0.00b | 0.02 ± 0.00a | 0.04 ± 0.00b | n.d. |
| 1,5,7-Trimethyl-1,2,3,4-tetrahydronaphthalene | 3.74 ± 0.10d | 0.36 ± 0.01b | 2.46 ± 0.12c | 0.05 ± 0.01a |
| 1,1,5-Trimethyl-1,2-dihydronaphthalene | 0.48 ± 0.01d | 0.23 ± 0.01b | 0.41 ± 0.01c | 0.02 ± 0.01a |
| Tridecane | 0.84 ± 0.02c | 0.07 ± 0.00a | 0.26 ± 0.01b | 0.08 ± 0.01a |
| Dodecane | 0.09 ± 0.00a | n.d. | n.d. | n.d. |
| Styrene | 37.90 ± 0.60c | 14.57 ± 0.33b | 36.32 ± 1.07c | 2.62 ± 0.52a |

Note: n.d., Not detected; mean values in lines with different letters are significantly different ($p < 0.05$).

the impurities in agricultural distillates and improve the sensory quality of spirits.

The experiments described in this work were carried out using the batch system, which may be cumbersome when scaled up in a manufacturing plant.

An alternative is to apply a continuous, counter-current, adsorbent-liquid flow through a column or several columns in series. However, further research would be required to optimise the conditions for such a continuous process.

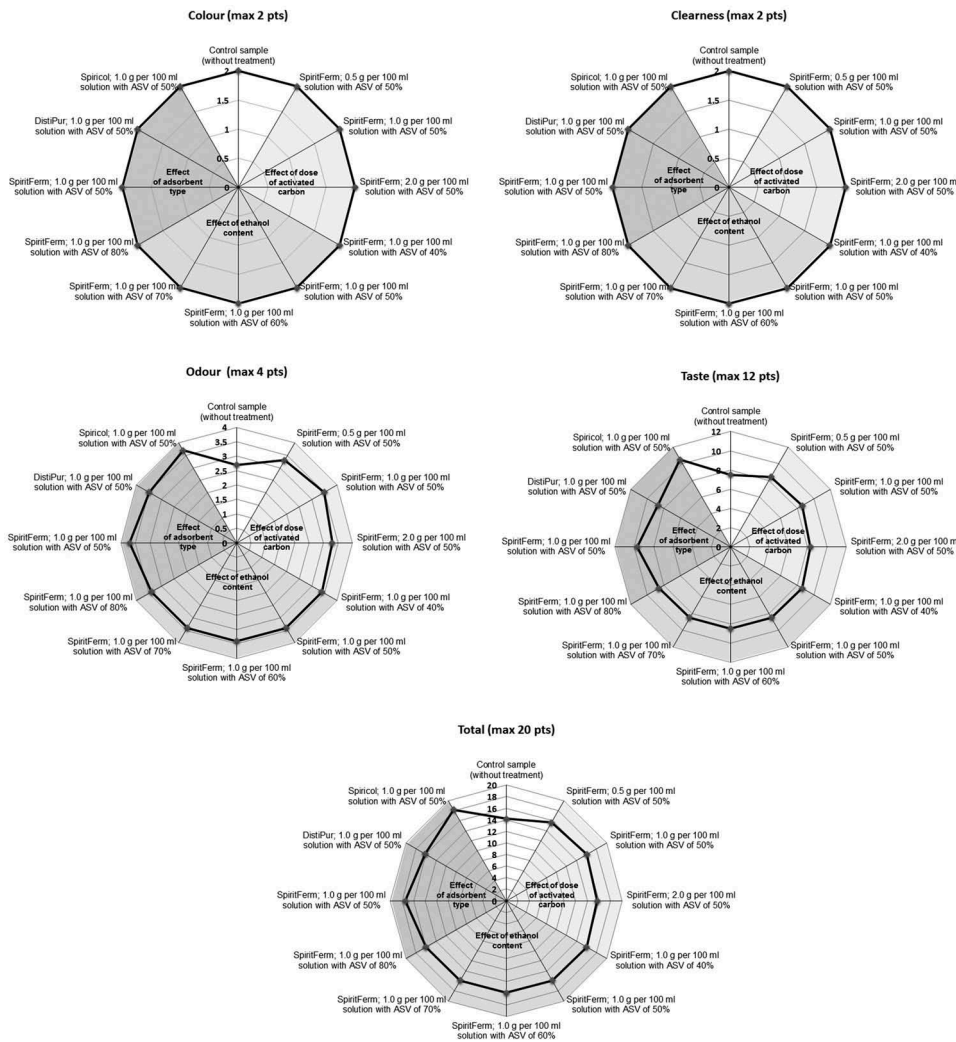


Figure 1. Organoleptic assessment of tested samples of agricultural distillate.

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No potential conflict of interest was reported by the authors.

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