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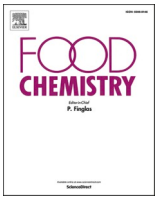

Comprehensive analysis of risk factors (methanol, acetaldehyde and higher alcohols) in alcoholic beverages and their reduction strategies: GC–MS analysis and modified activated carbon adsorption and characterization

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ABSTRACT

This study endeavors to examine the levels of risk factors in alcoholic beverages and propose mitigation strategies. GC–MS analysis was utilized to assess risk factors in various distilled-spirits. The content of such risk factors in spirits ranked as follows: vodka ≈ gin < baijiu < whiskey < brandy, and all were adhering to the Chinese national standard. Additionally, a method was refined to alleviate these risks, employing various reagents for activated carbon modification and evaluating their adsorption efficiency for risk factors reduction. Oxalic acid-modified activated carbon exhibited promising adsorption rates for risk factors with acceptable flavor compounds loss, rendering it a prospective solution for health hazard reduction. Characterization via SEM and nitrogen-adsorption-desorption was conducted on the optimal material, complemented by sensory experiments to optimize its application. This study offers valuable insights into the content of risk factors in alcoholic beverages, aiding in improving quality and safety of alcoholic beverages.

1. Introduction

Alcoholic beverages constitute a crucial element of cultural, social, and ceremonial activities. However, there is an increasing focus on the safety implications of these beverages and some of the unavoidable risk factors associated with them are gradually gaining attention (Yang, Zhang, & Guo, 2022).

Research has demonstrated that “higher alcohols” play a pivotal role in beverages and alcoholic drinks. Appropriate concentrations of these compounds are known to enhance the overall flavor profile of beverages and contribute to the harmonization of their composition (Lachenmeier, Haupt, & Schulz, 2008). However, an excessive presence of higher alcohols in beverages can lead to the development of undesirable odors, resulting in the manifestation of prominent side effects, such as increased thirst and headaches following consumption (Bai et al., 2011). This phenomenon is unfavorable for the health of the consumer (Lachenmeier et al., 2008). The formation of higher alcohols has been observed to be intricately linked to the fermentation temperature. This relationship has been established and verified in various beverages such as beer, fruit wine, and liquid fermented baijiu (Buckee, 1992; Lee, Yu, Curran, & Liu, 2011). Higher alcohols are considered natural by-products resulting from the standard metabolic processes of yeast during liquor brewing (Yoshizawa, 1999). Their production occurs through two primary pathways. Firstly, yeast utilizes amino acids as substrates in the catabolic pathway, while secondly, in the anabolic pathway, yeast employs sugar as the substrate to synthesize these compounds (Hazelwood Lucie, Daran, van Maris Antonius, Pronk Jack, & Dickinson, 2008). In comparison to ethanol, the oxidation rate of higher alcohols in the human body is relatively sluggish, leading to prolonged residence periods within the body (Lachenmeier et al., 2008). Consequently, this delayed oxidation may result in symptoms such as dizziness, neuralgia, and severe headaches (Procopio, Qian, & Becker, 2011). The prevalent

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issue of elevated levels of higher alcohols in traditional brewing methods has garnered significant attention within the industry, prompting widespread concern.

Another risk factor, acetaldehyde, is classified as a carcinogenic compound (Secretan et al., 2009). In alcoholic beverages, acetaldehyde primarily originates from the enzyme-catalyzed decarboxylation of pyruvate during fermentation, facilitated by pyruvate decarboxylase. Acetaldehyde is a significant flavor component detectable in various types of alcoholic beverages, including red wine, baijiu, and beer (Yisong Liu et al., 2022). However, elevated acetaldehyde concentrations not only adversely affect the flavor of alcoholic beverages but also pose a health risk (Saison et al., 2010). After a single dose (0.5 g/kg body weight) of ethanol, peak concentrations of acetaldehyde in saliva ranged from 18 to 143 μM (Homann, Jousimies-Somer, Jokelainen, Heine, & Salaspuro, 1997). Drinking alcohol with higher levels of acetaldehyde leads to a significantly higher concentration of acetaldehyde in saliva and an increased risk of upper digestive tract cancer (Linderborg, Salaspuro, & Väkeväinen, 2011). Studies indicate that acetaldehyde exhibits greater toxicity to the human body compared to ethanol (Lachenmeier, Kanteres, & Rehm, 2009).

Methanol represents an additional toxic compound present in alcoholic beverages. It is the primary causative agent responsible for poisoning incidents. According to documented statistics spanning the period from 2017 to 2019, 7104 cases of methanol poisoning were reported worldwide, resulting in 1888 fatalities. Notably, over 90% of these incidents occurred among individuals of Asian descent, with 41% falling within the age range of 25 to 36 years old. Furthermore, 93% of the affected individuals were male (Abegg, Magro, van den Broek, Pratsinis, & Güntner, 2020). Humans possess a limited capacity to detoxify the sulfate anion generated as a by-product of methanol oxidation, rendering them highly susceptible to the toxic effects of methanol (Abbasi & Alizadeh, 2020). Methanol occurs naturally in most alcoholic beverages due to the degradation of pectin during fermentation (Anthon & Barrett, 2012; Dorokhov, Shindyapina, Sheshukova, & Komarova, 2015).

Numerous techniques have been devised to detect methanol, acetaldehyde and higher alcohols in diverse matrices, particularly in beverage products. These methods encompass high-performance liquid chromatography (HPLC) (Chen et al., 1998), gas chromatography (GC) (Wang, Wang, & Choong, 2004), electrochemical analysis (Gülce, Gülce, Kavanoz, Coşkun, & Yıldız, 2002), nuclear magnetic resonance (NMR) (Kuballa et al., 2018), Raman spectroscopy (Ellis et al., 2019) and gas sensors (van den Broek, Abegg, Pratsinis, & Güntner, 2019), each offering distinct levels of sensitivity. Presently, gas chromatography–mass spectrometry (GC–MS) is the gold standard for the quantitative determination of methanol and higher alcohols in alcoholic beverages (Januszek, Satora, & Tarko, 2020; Oliveira do Nascimento et al., 2022; Perestrelo, Caldeira, Rodrigues, Pereira, & Câmara, 2022). Qin et al. (Qin et al., 2023) conducted a study employing headspace solid-phase microextraction coupled with GC–MS to investigate the aroma-active compounds in sesame aroma baijiu; higher alcohols in these three types of sesame aroma baijiu ranged from 0.32 mg/L to 255.39 mg/L. Li et al. (H. Li et al., 2019) adopted the concept of molecular sensory science, including aroma extract dilution analysis based on gas chromatography-olfactometry combined with GC–MS, to identify key odorants in Guojing sesame aroma baijiu. The concentration of n-butanol was found to range from 141.75 mg/L to 280.00 mg/L, while the content of n-hexanol fell within the range of 27.25 mg/L to 36.53 mg/L.

After obtaining the content of risk factors, it is equally important to effectively reduce them, when needed. Currently, conventional commercial activated carbon is frequently employed for adsorbing and removing such risk factors present in baijiu. Nevertheless, studies have indicated that modified activated carbon exhibits superior adsorption efficacy concerning higher alcohols compared to the regular activated carbon (Hong, Hu, Shiue, Chen, & Leggett, 2022). However, the research on modified activated carbon mainly focuses on gas adsorption (Oguz Erdogan & Kopac, 2023; B. Zhang et al., 2015), while the adsorption in alcoholic beverages directly is less studied. Turkan et al. (Oguz Erdogan & Kopac, 2019) investigated the adsorption of isopropanol, acetone and ethanol vapors on modified activated carbon, and found that chemically-modified activated carbons could effectively improve the adsorption capacity of organic vapors. Zhang et al. (Zhang et al., 2023) used activated carbon adsorption to purify and recover short chain alcohols and acids in wastewater. By comparing the adsorption capacities of four different activated carbons, an activated carbon with the highest adsorption capacity (196.2 mg/g) for mixed short chain alcohols and acids in waste water was obtained. Hong et al. (Hong et al., 2022) modified activated carbon with organic acids and explored its adsorption capacity for isopropanol. The results showed that the surface area of oxalic acid-modified activated carbon was significantly increased compared to ordinary activated carbon, and oxalic acid groups were added on the surface of activated carbon, which strengthened the adsorption capacity for isopropanol.

Gaining comprehensive insights into the variation in occurrence of risk factors in alcoholic beverages during distillation and storage, and implementing an efficient and environmentally friendly approach to effectively mitigate these risk factors, is significant in offering process guidance for alcoholic beverage manufacturers and enhancing the safety of such products. Concurrently, analyzing the content of risk factors in commercially available distilled spirits holds implications for consumers in their pursuit of safer alcohol consumption choices. In this study, we conducted qualitative, and quantitative analyses of risk factors in diverse types of base baijiu, commercially available baijiu with different aromas, and various types of distilled spirits. Employing a rapid and precise direct injection GC–MS method, we quantitatively investigated these risk factors. Subsequently, two commonly used commercial activated carbons were subjected to modification using eight different solvents, and the adsorption capacity of the modified activated carbon towards risk factors in baijiu was analyzed. This allowed us to identify the most optimal modification reagent for further optimization. This research thus provides process guidance and effective methodologies for mitigating risk factors in alcoholic beverage production.

2. Materials and methods

2.1. Chemicals and materials

All prepared solutions are expressed in terms of volume percent (%, *v*/v), unless otherwise specified. Except for acetaldehyde (purity ≥97%), the purity of all reagents was over 99%. Acetaldehyde, methanol, propanol, butanol, isobutanol, n-pentanol, isopentanol, 2-methyl-1-butanol, n-hexanol, phenethyl alcohol, sulfamic acid, benzoic acid, oxalic acid, formic acid, tartaric acid, citric acid, NaOH and salicylic acid were purchased from J&K Scientific Co., Ltd. (Beijing, China). All water used in this experiment was from the Mili-Q ultrapure water system (C85358, Germany).

Tris-HCl, potassium dihydrogen phosphate, dipotassium hydrogen phosphate, NAD^+, acetaldehyde dehydrogenase (ALDH) and dithiothreitol (DTT) were purchased from Sigma-Aldrich Scientific Co., Ltd. (Shanghai, China). Two types of activated carbon (granular and powdery) were purchased from Mreda Scientific Co., Ltd. (Beijing, China).

2.2. Samples

The following samples were analyzed (total 159 different samples, obtained from different manufacturers in China): (i) light aroma base baijiu from north of China with eleven different storage times (new base

baijiu; 1–10 years); (ii) light aroma base baijiu from west of China with 19 different storage times (new base baijiu; 1–11 months; 1–7 years); (iii) sauce aroma base baijiu from south of China with 19 different distillation times (samples were taken every two minutes during the distillation process); (iv) 80 commercial baijiu (17 sesame aroma baijiu, 20 strong aroma baijiu, 20 sauce aroma baijiu and 23 light aroma baijiu); (v) 30 other distilled spirits (9 whiskies, 8 vodkas, 7 gins and 6 brandies).

2.3. Quantitative analysis of risk factors by direct injection with GC–MS

All distilled spirit samples were filtered using a 0.22 μm Syringe filter, and ~ 1 μL of the sample was used for GC–MS analysis. GC–MS analyses were performed on an Agilent 7890B GC and Agilent 5977 A MSD with a DB-WAX column (60 m × 0.25 mm i.d., 0.25 μm film thickness, J&W Scientific, USA). The oven temperature was initially at 40 °C, held for 3 min, increased to 130 °C (held for 2 min) at 2 °C/min, ramped to 220 °C (held for 1 min) at 20 °C/min. The electron ionization energy was 70 eV, and the ion source temperature was 220 °C. The split ratio was 15:1 and the split flow was 15 mL/min. The *m/z* full-scan range was 15–350.

Quantitative analysis was performed by external standard method. Mixed solutions of risk factors with different concentrations were prepared in a 45% ethanol solution in water. Given the variation in the content of each risk factors in alcoholic beverages, ensuring accurate quantification required the utilization of standard curves encompassing an appropriate concentration range for each specific compound. It is important to avoid an excessively broad concentration range, as this may compromise the accuracy of quantification. To address this, two standard curves were constructed for each toxic compound, each tailored to accommodate its distinct concentration range. Each sample was injected three times, detection limit was defined as the concentration of the compound at which the signal-to -noise ratio was 3.

The samples were analyzed with heat maps and clustered. In the heat map, a *Z*-score is used to measure the degree of dispersion of data.

$$Z\ Score = \frac{X - \overline{X}}{s} \tag{1}$$

X represents the raw data, $\overline{X}$ represents the mean of the data, and s represents the standard deviation. When the Z-score is larger, it means that the data is futher away from the average.

2.4. Effect of risk factors on ALDH

Acetaldehyde and nicotinamide adenine dinucleotide (NAD^+) (coenzyme I) are converted into acetate and NADH (reduced coenzyme I) under the action of ALDH, and NADH has an absorption peak at a wavelength of 340 nm. In order to compare the effects of different risk factors on acetaldehyde dehydrogenase, solutions of the different risk factors with concentrations of 10, 50, 100, 200, 500, 800, and 1000 mg/L were prepared in 45% vol edible alcohol and 300 mg /L acetaldehyde.

In a 200 μL reaction system, the following components were added sequentially: 90 μL of 0.1 mol/L phosphate-buffered saline (PBS), 10 μL of 0.4 mol/L DTT, 55 μL of 4 mmol/L NAD^+, 30 μL of 2 U/mL ALDH solution (thawed beforehand), and 15 μL of the previously mentioned solution containing higher alcohol, ethanol, and acetaldehyde. Prior to the addition of samples, the microplate reader was preheated for 30 min. Subsequently, the samples were added to the microplate in the designated order, followed by incubation in a 37 °C incubator for 5 min. The absorbance value was measured at a wavelength of 340 nm by microplate reader (Thermo Fisher, USA). Using the enzyme activity as the ordinate and the ALDH activity as the abscissa, a standard curve of ALDH was constructed. Each experiment was repeated three times, and each sample was tested three times.

2.5. Modification and optimization of different activated carbon

Eight different modification reagents were dissolved in water at the concentrations shown in the Supporting Information (SI), Table S1. These solutions were mixed with activated carbon in separate flasks and stirred at a constant temperature of 25 °C using a collector-type constant temperature heating magnetic stirrer for 1 h. After that, the entire solution was decanted, and the activated carbon was thoroughly washed with deionized water five times. The resulting modified activated carbon was then dried in a vacuum oven at 100 °C to obtain the desired product.

For optimization, activated carbon was subjected to modification using various concentrations of oxalic acid solutions, and the ability of the modified activated carbon to adsorb various risk factors was evaluated.

2.6. Adsorption test of risk factors by modified activated carbon

A precise mass of 1.00 g of activated carbon was measured and introduced into either simulated spirit (risk factors standard solution, 45% ethanol) or a base baijiu at a solid-to-liquid ratio of 1:10 (m/v). Subsequently, the mixture was allowed to sit still for a duration of 4 h. After the specified time, the supernatant from the base baijiu was filtered and collected to determine the ethanol concentration by refractometer (Thermo Fisher, USA). Additionally, the analysis of risk factors (methanol, acetaldehyde, and higher alcohols), esters, and acids was conducted using GC–MS.

Formula 2 was used to calculate the adsorption rate of risk factors from simulated spirit, C referred to concentration. Formula 3 was used to calculate the reduction of risk factors per loss of acids or ester compounds in real baijiu.

$$Adsorption\ ratio\ (\%) = \frac{C_{Pre-adsorption}}{C_{Post-adsorption}} \tag{2}$$

$$Adsorption\ rates\left(\frac{risk\ factors}{flavor\ compounds}\right)(\%) = \frac{Adsorption\ ratio_{risk\ factors}}{Adsorption\ ratio_{flavor\ compounds}} \tag{3}$$

Log_2FC (log_2 fold change) was used quantify the difference between the activated carbon 1 and activated carbon 2 under the same conditions. This value is obtained by taking the logarithm base 2 of the ratio of the variables in activated carbon 1 and activated carbon 2 (formula 4). The p value was used to measure the significant difference (Duncan-test) between the groups. When $p < 0.05$, the data between the groups were considered to have significant differences.

$$Log_2FC = log_2\frac{Var_2}{Var_1} \tag{4}$$

Var_2 is a variable for activated carbon 2 and Var_1 is a variable for activated carbon 1.

2.7. Structural characterization of activated carbon

The morphological characteristics of the activated carbon samples were analyzed using Scanning Electron Microscopy (SEM) on an SU-8010 instrument (HITACHI, Japan). The samples were securely affixed to mounts using conductive adhesive and subsequently coated with a thin layer of gold via ion beam deposition for one minute. Observations were conducted at an accelerating voltage of 3.00 kV across various magnifications.

Prior to analytical assessment, a 50 mg portion of each sample underwent a desiccation procedure lasting 12 h. Following desiccation, the specimen was transferred to the analysis chamber, where vacuum degassing and subsequent thermal conditioning at 300 °C for 8 h were conducted until the internal pressure reached equilibrium below 10 Torr. Subsequent analyses were performed using an AUTOSORB-IQ2-MP specific surface and micropore size analyzer (Quantachrome, USA). Nitrogen adsorption-desorption isotherms were generated at a temperature of −196 °C. Analytical methodologies, including the Brunauer-Emmett-Teller (BET) method, t-Plot, and classical Density Functional Theory (DFT), were utilized to determine the specific surface area, and pore size distribution of the activated carbon.

2.8. Sensory analysis

In order to systematically investigate the effectiveness of augmented activated carbon in enhancing the quality of baijiu, varying concentrations of activated carbon were integrated into a standardized baijiu formulation to facilitate the adsorption of potential impurities. Sensory evaluations were conducted under controlled thermal conditions, maintaining a temperature of 20 ± 1 °C, and involved a demographic-balanced cohort of 16 trained panelists with an average age of 26 years.

A 20 mL aliquot of sesame-flavored base baijiu, comprising 52% alcohol by volume, was dispensed into a designated vessel for olfactory assessment. During sensory analysis, panelists positioned the glassware beneath their nose and performed uniform inhalations above the liquid phase. Following olfactory evaluation and collective deliberation, a set of eight prominent aromatic attributes was identified: ethyl hexanoate (fruitiness), acetic acid (acidity), dimethyl trisulfide (rancid), ethanol (alcohol), toasted sesame (roasted characteristics), steamed sorghum (grain), γ-nonalactone (sweetness), and ethyl 3-phenylpropanoate (floral) (H. Li et al., 2019). Solutions of these compounds or steamed sorghum were used to evaluate different aroma properties in baijiu.

Subsequently, panelists participated in calibration sessions elucidating the eight identified aromatic descriptors alongside their corresponding reference compounds. Assessors were instructed to assess aroma intensities using a 21-point graded scale, ranging from 0 to 10, with demarcations at 0.5-unit intervals. The scoring criteria were as follows: 0 indicating non-perceptibility, scores between 1 and 4 denoting low aromatic intensity, scores of 5 to 7 representing moderate intensity, and scores between 8 and 10 classified as high aromatic intensity.

2.9. Data visualization

Column charts were drawn using GraphPad 8.0. Radar charts were drawn using Origin 2018. Heat map analysis was constructed using the OmicStudio tools at https://www.omicstudio.cn/tool.

3. Results and discussions

3.1. Standard curves of risk factors

To ensure the accuracy of quantitative analysis, given the diverse range of spirits and flavor types tested, two standard curves were constructed for the tested compounds exhibiting significant variations in content (see SI, Table S2).

3.2. Quantification of risk factors in base baijiu

Samples were collected during the commencement of baijiu distillation, and subsequently, at 2 min intervals throughout the process. All samples were subjected to analysis using GC–MS, and the alterations in risk factors were monitored (SI, Fig. S1). The contents of acetaldehyde, methanol, propanol, 2-methyl-1-butanol and isopentanol were the highest, and showed a decreasing trend with the extension of distillation time. Since acetaldehyde and methanol cannot form an azeotrope with water, a large number of acetaldehyde and methanol are distilled after the temperature reaches the boiling point of acetaldehyde and methanol respectively in the early stage of distillation, and then the content drops sharply. Different from the above compounds, the contents of isobutanol, n-butanol and n-pentanol were relatively high at the initial stage of distillation, and with the extension of distillation time, their contents showed a trend of first decreasing, then increasing, and finally decreasing again. This is due to the fact that as the temperature increases, they are gradually distilled out, but as the temperature continues to rise they gradually form an azeotrope with water, resulting in reduced distillate. It is worth noting that the content of n-hexanol is relatively high in the middle stage of baijiu distillation. In addition, the phenylethyl alcohol content increased with the extension of distillation time. This is due to the relatively high boiling point of compounds with more complex structures, and the main distillate at the early stages of distillation constitutes low-boiling-point compounds. The average content of isobutanol, acetaldehyde, propanol and isopentanol were the highest in the process of baijiu distillation.

In the traditional Chinese baijiu brewing process, a significant operation known as “cutting-out both ends of the distillate” involves discarding the initial and final portions of the baijiu distillation process. Based on the experience of distilleries, it is common to select a certain period of baijiu. This time period typically is two minutes after the start of distillation and stops 25 min after the start of distillation. This technique effectively reduces the content of risk factors in baijiu, especially methanol. Furthermore, during the middle stage of baijiu distillation, the content of linear alcohols was higher, thereby contributing to the enhanced flavor of baijiu (Lachenmeier et al., 2008).

GC–MS analysis was conducted on samples of a specific light aroma baijiu stored for varying durations (SI, Fig. S2). The contents of acetaldehyde, isobutanol, isopentanol, 2-methyl-1-butanol and phenylethyl alcohol increased with the increase of storage time. On the contrary, the contents of methanol, butanol and hexanol decreased with the extension of storage time. This may be due to the small chemical hindrance of straight-chain alcohols compared with branched-chain alcohols, which are more likely to react with acids to form esters. The content of n-pentanol increased at the later stage of storage, but the average content was only 4.76 mg/L during the whole storage process. The content of n-propyl alcohol decreased at the beginning of storage, but increased significantly when the storage time exceeded 5 years. For risk factors with higher average content during storage, the content of 2-methyl-1-butanol, isobutanol, acetaldehyde, isopentanol and propanol all increased after 5 years of storage. Therefore, it is suggested that the light aroma baijiu should not be stored for too long. It is recommended to consume within five years to preserve the desired aroma characteristics and to avoid rising risk factor levels.

GC–MS analysis was performed on samples of another light aroma baijiu, stored for different durations (SI, Fig. S3). The main difference between the previous and this specific baijiu is that different raw materials were used in the production. Specifically, the second type incorporated peas into the jiuqu (fermentation starter rich in microorganisms), leading to higher pectin content compared to wheat. The contents of methanol, phenylethanol and n-butanol were the highest in the first year of storage, and then decreased with the increase of storage time. The contents of isobutanol, isopentanol and 2-methyl-1-butanol showed a similar trend, increasing slightly in the first year and then decreasing, and increasing continuously in the 2nd to 7th year. The

content of acetaldehyde increased first and then decreased. With the extension of storage time, the contents of propyl alcohol, n-pentanol and n-hexyl alcohol showed a trend of first increasing and then decreasing, and they all reached the maximum value at 4 years of storage. The difference between the trends in the two different light aroma baijiu as shown in Figs. S2 and S3 may be attributed to the difference in raw materials used in the production of the two types of light aroma baijiu. There are many variations in other parameters, including raw materials, microbial communities, storage humidity and temperature. However, with the storage time of >5 years, the content of branched-chain alcohols such as isopentanol, isobutanol, 2-methyl-1-butanol increased strongly. This result validates the conclusion that light-flavored baijiu should not be stored for a long period of time, as it may lead to undesirable changes in its composition and aroma properties, while increasing the safety concerns of baijiu.

3.3. Quantification of risk factors in different distilled sprits

Fig. 1 shows heat maps of the risk factors in 120 distilled spirits (whisky, vodka, gin, brandy and 4 different aroma baijiu), and it is clear that the main risk factors in whiskey and brandy are phenylethanol, isobutanol, isopentanol, and 2-methyl-1-butanol. The risk factors in baijiu are mainly distributed in the red box, that is, straight-chain alcohols. This may be due to the difference of raw materials, fermentation process and storage process. The multi-microbial fermentation of spirits production helps to reduce the amount of isopentanol, isobutanol and propanol. For storage, brandy and whiskey are mainly stored in oak barrels, which might lead to a substantial increase in isopentanol and isobutanol content (Alcarde, Souza, & Bortoletto, 2014), while baijiu is mainly stored in pottery jars.

As shown in SI, Fig. S4, the content of higher alcohols in sauce aroma baijiu is generally lower than in the other three kinds of baijiu, probably because the process of sauce aroma baijiu is carried out at high temperature, which weakens the proliferation of yeast, thus weakens the catabolic pathway of amino acid and amino acid sugar synthesis, and leads to a lower content of higher alcohols (Meng, 2016). The main risk factors of light aroma baijiu are branched alcohol (red box), Strong aroma baijiu and sauce aroma baijiu contain mainly straight chain alcohols (blue and green box), and the risk factors of sesame aroma baijiu are wider, but importantly n-hexanol, n-butanol, n-pentanol, isobutanol and phenylethyl alcohol.

3.4. The effect of risk factors on ALDH

Acetaldehyde is a product of ethanol metabolism in the human body. Excessive accumulation of acetaldehyde can cause arrhythmia and nausea (Umulis, Gürmen, Singh, & Fogler, 2005). The effect of higher alcohols on ALDH directly affects a person's degree of intoxication. As shown in Fig. 2, the enzyme activity of ALDH showed relatively stable

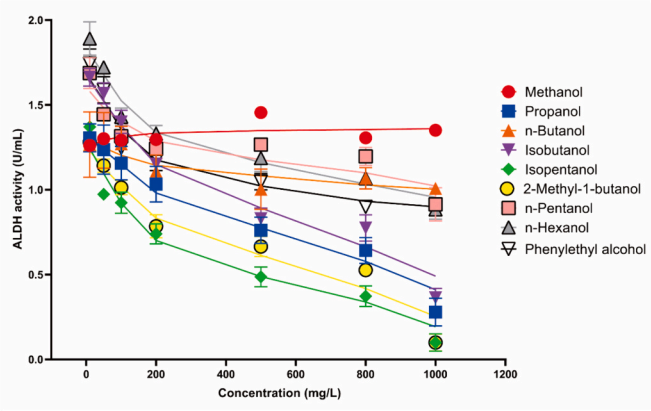

Fig. 2. Impact of risk factors on ALDH. Risk factors concentration: 10 mg/L-1000 mg/L (n = 9).

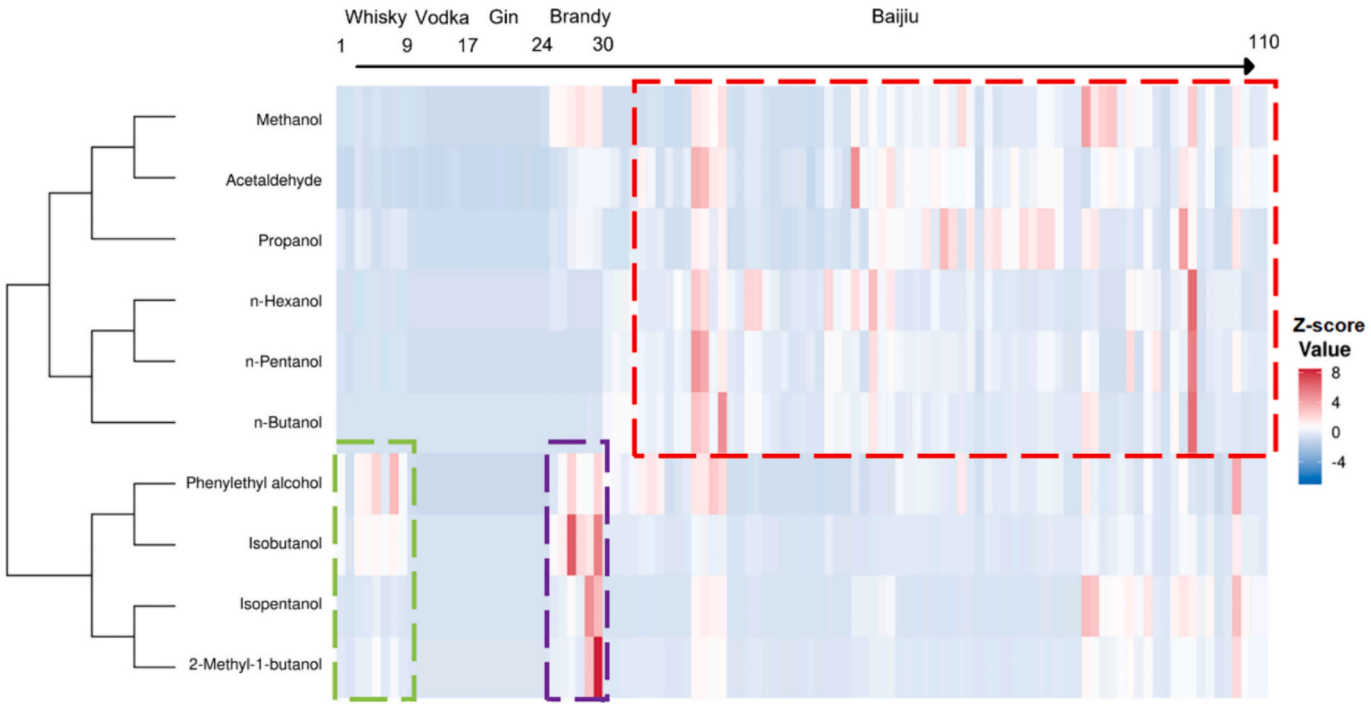

Fig. 1. Content of risk factors in 5 different distilled spirits (n = 110) Z-scores are used to show the relative abundance of each risk factor in different spirits. Cluster analysis was used to group risk factors that vary similarly.

behavior with the increase of methanol concentration. Conversely, as the concentration of other higher alcohols increased, their inhibitory effects on ALDH gradually intensified. Among these higher alcohols, isopentanol exhibited the most substantial effect on ALDH activity, followed by 2-methyl-1-butanol. With the exception of n-propanol, other straight-chain higher alcohols had lesser effects on ALDH compared to isopentanol, 2-methyl-1-butanol, and isobutanol. It was observed that branched-chain alcohols exerted a more pronounced impact on ALDH, suggesting that they might induce dizziness.

3.5. Adsorption of risk factors by different modified activated carbon

Fig. 3 shows that activated carbon 2, treated with oxalic acid is the most effective in reducing acetaldehyde, propanol and n-pentanol. The activated carbon 2 modified by benzoic acid and citric acid showed obvious adsorption of methanol. Oxalic acid and NaOH modified activated carbon 2 also have the best adsorption properties for isobutanol, isopentanol, 2-methyl-1-butanol and n-pentanol, which can effectively reduce branched chain alcohols in simulated samples. For n-butanol and n-hexanol, NaOH modified activated carbon 2 has the best adsorption effect. Except for benzoic acid and salicylic acid, the adsorption effect of other modified activated carbons on phenethyl alcohol was better. The Log_2FC values of all risk factors are >0, which shows that the adsorption of all risk factors by modified activated carbon 2 was greater than that by activated carbon 1. The modified activated carbon 2 showed good adsorption effects ($Log_2FC > 1$) on propanol acetaldehyde and methanol, and the difference was significant. In summary, oxalic acid modified activated carbon 2 has higher adsorption efficiency for risk factors in simulated samples. This may be because oxalic acid is a fairly strong organic acid, which further destroys the pores on the surface of activated carbon, leading to the formation of micropores, thus enhancing the adsorption capacity (Hong et al., 2022).

3.6. Residual content of esters, acids and ethanol after use of modified activated carbon

Esters and acid compounds play a crucial role in the flavor of distilled spirits (Li et al., 2023; Xu et al., 2022). Fig. S5, SI shows the heat map and bubble map of residual content of important esters and acids after use of modified activated carbon. The Log_2FC values of all flavor components except acetic acid and butyric acid were >0, which shows that the modified activated carbon 1 only retained acetic acid and butyric acid more strongly than activated carbon 2. NaOH modified activated carbon has poor residual effect on acid, which is due to the existence of alkaline groups on the surface of alkali modified activated carbon, which can be well combined with acid (Liu et al., 2014). In general, salicylic acid modified activated carbon have the best ester residual characteristics, citric acid and tartaric acid modified activated carbon have the best acid residual characteristics. This may be because the acidity of citric acid (pKa1 = 3.14) and tartaric acid (pKa1 = 3.04) is weak, so the degree of damage to the surface of activated carbon is limited (Gao, Li, Gao, & Tai, 2007). However, citric acid contains three carboxyl groups, and tartaric acid contains two carboxyl groups, which will introduce carboxyl groups to the surface of activated carbon, resulting in a decrease in acid adsorption capacity.

3.7. Reduction of risk factors by per equivalent of acid or ester lost

Through the analysis of the reduction efficiency of modified activated carbon on risk factors and the residual content of esters and acids, two types of significant flavor-contributing compounds in baijiu, the optimal modified activated carbon that effectively removes risk factors while minimizing the loss of flavor compounds can be identified. Fig. S6 shows the ratio by dividing the removal of risk factors by the removal of esters or acids (formula 3). Among the tested modifications, oxalic acid-modified activated carbon-2 exhibited the highest capacity for reducing higher alcohols while causing the least reduction in esters. Furthermore,

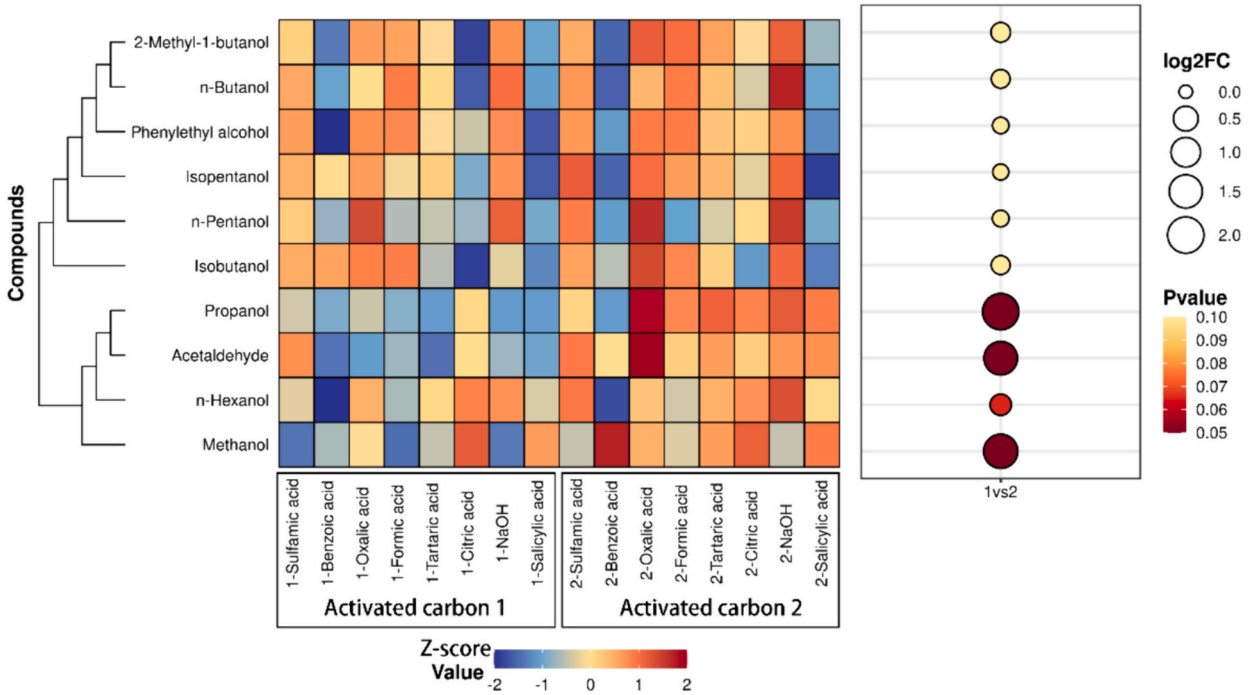

Fig. 3. Adsorption by modified commercial activated carbon of risk factors. *Z*-scores show the relative adsorption of risk factors for different types of activated carbon and reagent. The size of bubbles in the bubble diagram is the average log_2FC value between groups of adsorptions of risk factors by activated carbon 1 and activated carbon 2, and the color of bubbles indicates whether differences between group 1 and 2 were significant.

it also demonstrated effective reduction of acetaldehyde with acceptable loss of esters and acids. Citric acid and tartaric acid modified carbon also exhibited favorable reduction of higher alcohols with acceptable loss of acids. For methanol, citric acid modified carbon showed the most efficient removal while maintaining the acceptable loss of acids and esters. Based on the analysis of methanol content in base baijiu and distilled spirits, it was found to be well within the Chinese national standard (≤ 600 mg/L). Notably, esters play a pivotal role in baijiu flavor (Xu et al., 2022), and oxalic acid modified activated carbon demonstrated the most effective adsorption of risk factors among all tested activated carbons.

3.8. Optimization of oxalic acid modified activated carbons

As depicted in Fig. S7(a), the modified activated carbon 2 treated with oxalic solutions ranging from 0.2 to 1 mol/L exhibited maximum reduction of higher alcohols with acceptable loss of esters. Notably, the 1 mol/L oxalic acid modified carbon 2 demonstrated significant reduction of higher alcohols with the lowest loss of acids. Additionally, Fig. S7 (b) illustrated that the 1 mol/L oxalic acid modified carbon 2 was effective in reducing acetaldehyde with the acceptable loss of both esters and acids. Furthermore, for methanol adsorption, Fig. S7(c) revealed that the 0.2 mol/L oxalic acid modified carbon 2 was well-suited for this purpose, as it resulted in acceptable loss of esters. On the other hand, the activated carbon 2 modified with 1 mol/L oxalic solution showed optimal adsorption of methanol with acceptable loss of acids. Overall, based on the comprehensive analysis, it can be concluded that the most suitable concentration for activated carbon modification was 1 mol/L oxalic acid solution.

3.9. Characterization of activated carbon

3.9.1. SEM analysis

Fig. S8 illustrates the pore structure of unmodified activated carbons (a-c) and modified activated carbons (d-f). As depicted in Fig. S8 (a-c), the surface of the unmodified activated carbon exhibits relatively uniform pores, whereas these pores become enlarged due to oxalic acid modification (Fig. S8 (d-f)). This is attributed to the introduction of oxalic acid, which disrupts the surface of the activated carbon, leading to an increase in pore volume.

3.9.2. Specific surface area and pore size analysis

As depicted in Fig. 4(a), when the relative pressure (P/P0) is <0.1, nitrogen adsorption rapidly increases with increasing relative pressure. This behavior is in accordance to the characteristics of Type I adsorption isotherms, indicating the presence of a wide range of porous networks in the waste grain activated carbon (Wei et al., 2019). In terms of pore structure, nitrogen molecules primarily permeate through micropores. A slender hysteresis loop is formed between the adsorption and desorption isotherms due to capillary condensation of the adsorbate, suggesting that the pore structure of waste grain activated carbon comprises a substantial amount of micropores as well as a considerable number of mesopores. As the relative pressure (P/P0) approaches 1, only the curve corresponding to the optimized activated carbon shows a marginal increase, indicating the presence of a limited number of macropores within the material.

To further investigate the pore structure distribution of waste grain activated carbon, DFT was employed to characterize its pore internal distribution, and the t-Plot method and Brunauer-Emmet-Teller (BET)

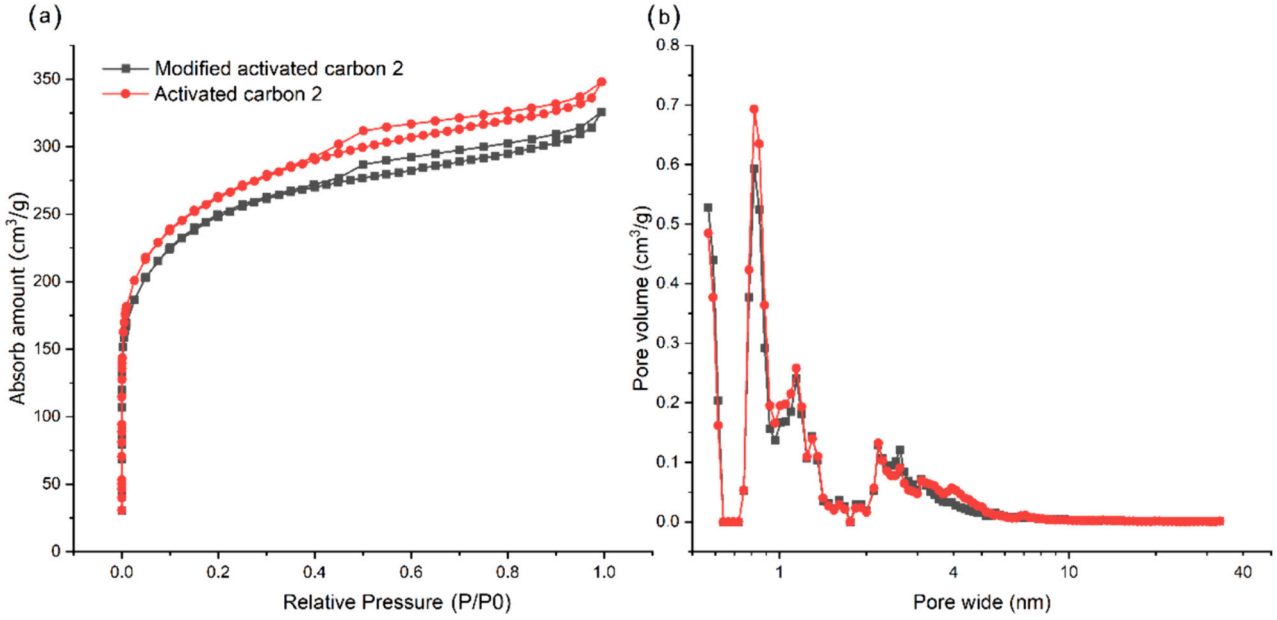

Fig. 4. N_2 adsorption isotherm curve of unmodified and modified activated carbon (a) and the DFT-based pore size distribution curve of unmodified and modified activated carbon (b).

Table 1
Characterization of activated carbon and modified activated carbon.

Activated carbons	Specific surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore diameter (nm)	Micropore volume (cm^3/g)	Micropore Surface area (m^2/g)
Modified Activated carbon 2	898.469	0.452	3.823	0.291	674.006
Activated carbon 2	953.167	0.484	3.408	0.296	688.662

method were utilized to evaluate its specific surface area, total pore volume, average pore diameter, and micropore volume, as shown in Fig. 4(b) and Table 1. From Fig. 4(b), it can be observed that the pore size distribution of activated carbon primarily falls within the range of 0.75–0.90 nm and 2–5 nm, confirming that its pore structure is mainly composed of micropores and mesopores. This observation aligns with the preceding analysis.

Oxalic acid modification decreases the BET specific surface area,

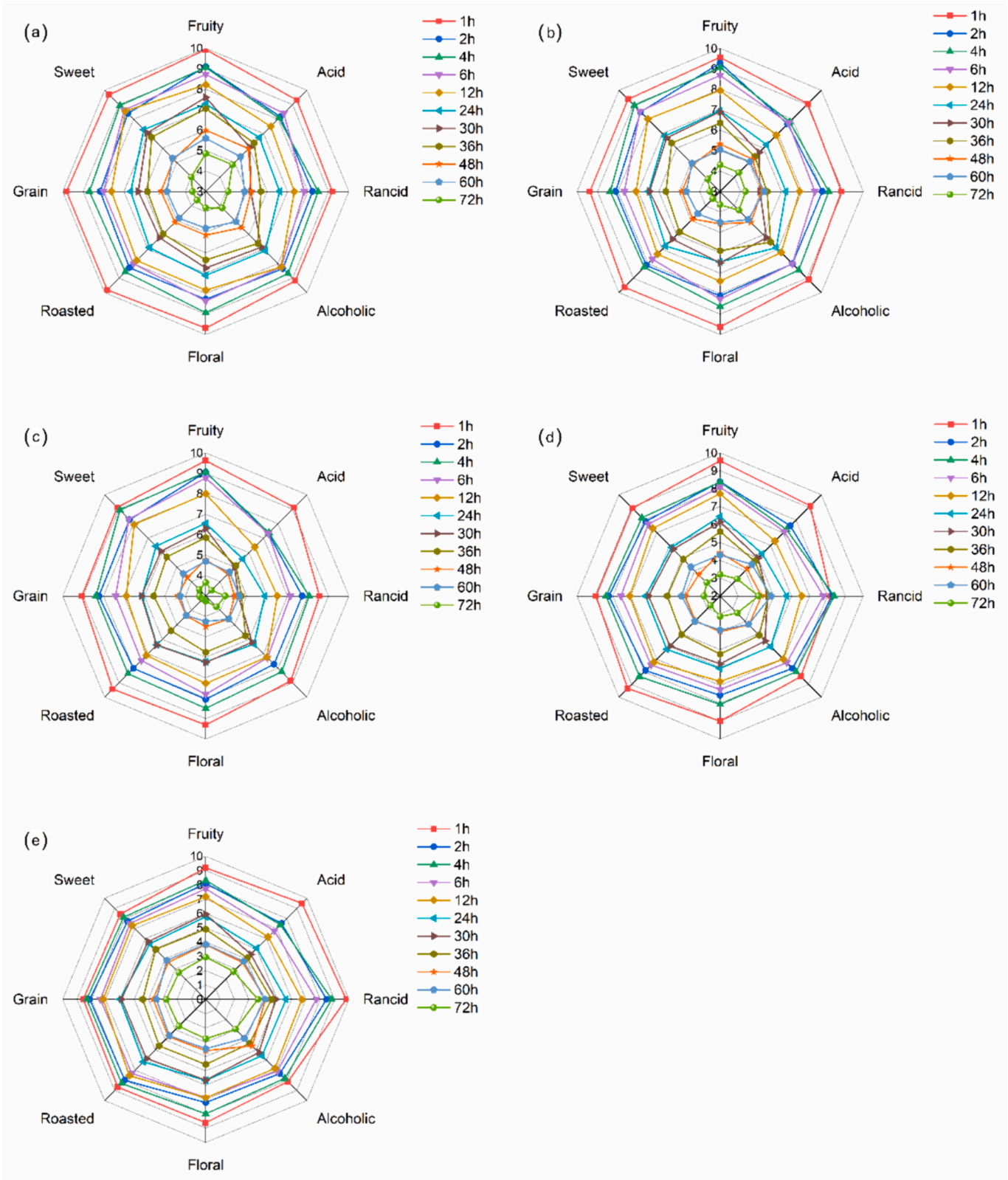

Fig. 5. The influence of activated carbon on the flavor of raw Baijiu under different adsorption times (1–72 h) and different amounts of activated carbon added (a: 0.05%; b: 0.15%; c: 0.25%; d: 0.50%; e: 1.00%, m/v).

total pore volume, micropore volume, and micropore specific surface area of the activated carbon. However, it is worth noting that oxalic acid modified activated carbon increased the proportion of micropore surface area and volume. For activated carbon 2, the micropore surface area and pore volume accounted for 72.24% and 61.16% of the total surface area and pore volume, respectively. For oxalic acid modified activated carbon 2, these two ratios rose to 75.02% and 64.38%. The adsorption of small molecules on oxalic acid modified activated carbon 2 was increased with the increase of the proportion of micropores.

3.10. Sensory analysis

Fig. 5 depicts the effect of oxalic acid modified activated carbon 2 on the sensory properties of baijiu at different intervals of a 72-h continuous adsorption. The observation results in Fig. 5 (a-e) show that there is an inverse relationship between the amount of activated carbon added and the characteristic flavor intensity of baijiu. A long adsorption time will lead to the decline of all flavor characteristics of baijiu. Fig. 5 (a-b) shows that in <1 h of adsorption time, the aroma fraction of the baijiu is stable at about 9 points, which indicates that the activated carbon has little influence on the overall aromatic characteristics of baijiu. Therefore, the optimal adsorption parameter is determined to be the duration of no longer than 1 h, and the activated carbon concentration is maintained below 0.15% (m/v). Under these conditions, the adsorbed baijiu was analyzed by GC–MS. The reduction efficiency of acetaldehyde is 10.63 ± 0.93%, and that of higher alcohols is 13.14 ± 3.13%.

4. Conclusions

The safety of alcoholic beverages has become a prominent area of concern. This study aims to explore the content and patterns of risk factors (methanol, acetaldehyde, higher alcohols) in alcoholic beverages and develop effective risk reduction strategies. GC–MS analysis was employed to investigate risk factors in base baijiu with varying distillation and storage times, commercial baijiu featuring diverse aroma profiles, and different distilled spirits. Additionally, a green and efficient modified activated carbon method was devised for targeted adsorption of risk factors in alcoholic beverages.

Results indicate that, with prolonged distillation time, all risk factors, except phenethyl alcohol, exhibited a declining trend. Notably, higher levels of branched alcohols were observed in the initial and final stages of distillation, whereas the middle stages showed higher levels of linear alcohols. For light aroma baijiu, the storage time should not be too long (>5 years). The average content ranking of risk factors (methanol, acetaldehyde and higher alcohols) in distilled spirits was found to be vodka ≈ gin < baijiu < whiskey < brandy, all adhering to Chinese national standards.

Modification of activated carbon was investigated using diverse reagents (oxalic acid, formic acid, tartaric acid, salicylic acid, sulfamic acid, citric acid, benzoic acid, and NaOH), evaluating their adsorption performance on risk factors. Oxalic acid-modified activated carbon exhibited the best adsorption rates on risk factors with acceptable losses of flavor substances (esters and acids). Consequently, oxalic acid-activated carbon emerges as a promising candidate for adsorbing risk factors in alcoholic beverages, effectively reducing the associated risks. The optimization of oxalic acid concentration demonstrated that using 1 mol/L for activated carbon modification yielded optimal adsorption results. The addition of oxalic acid was demonstrated to effectively enhance the adsorption performance of activated carbon through SEM and nitrogen adsorption-desorption analysis. Subsequently, optimal conditions for the use of oxalic acid-modified activated carbon were investigated through sensory experiments, revealing that the optimal conditions entail an activated carbon addition of <0.15% (*w/v*) and an adsorption time of <1 h. The reduction efficiency of acetaldehyde is 10.63 ± 0.93%, and that of higher alcohols is 13.14 ± 3.13%. These conditions are sufficient to effectively reduce the risk factors while maintaining the inherent flavor of baijiu.

This study aims to reveal the content of risk factors in alcoholic beverages and provide essential guidance to consumers. Additionally, the conclusions on the variation patterns of risk factors in base baijiu can significantly assist breweries in optimizing their processes, while the adoption of the eco-efficient risk factors adsorption method can enhance the safety of alcoholic beverages in breweries.

Ethical statement

Participants gave their consent to take part and use their information/data. Participants were able to withdraw from the survey at any time without giving a reason. Ethical approval for the involvement of human volunteers in this study was granted by Beijing Technology and Business University, Research Ethics Committee.

CRediT authorship contribution statement

Ziyang Wu: Writing – original draft, Visualization, Methodology, Conceptualization. **Silei Lv:** Visualization, Methodology. **Peng Xiao:** Visualization. **Gert IJ. Salentijn:** Supervision, Visualization, Writing – review & editing. **Huan Cheng:** Resources. **Hehe Li:** Supervision, Funding acquisition, Conceptualization. **Jinyuan Sun:** Resources. **Xingqian Ye:** Supervision, Resources. **Baoguo Sun:** Supervision, Resources.

Declaration of competing interest

There are no conflicts to declare.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodchem.2024.140461.

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