

## 多孔材料吸附技术改善中药挥发油稳定性的研究与应用

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**摘要:** 中药挥发油作为芳香类中药中的主要化学成分, 具有显著的抗菌、抗炎、抗氧化等药理作用。然而, 中药挥发油易挥发、易氧化变质等不稳定性问题严重限制了其制剂应用。多孔材料作为一种网格结构材料, 具有高比表面积、孔体积大、孔径可调、吸附能力强及表面化学性能可控等特点, 已被广泛应用于吸附分离、生物医学、工业催化、废水处理等领域。近年来利用多孔材料吸附挥发油, 为改善中药挥发油的稳定性提供了新的策略方法, 同时可实现中药挥发油的固化稳定与制剂应用。本文重点对介孔二氧化硅、介孔碳、介孔纳米羟基磷灰石、多孔金属有机框架、多孔淀粉等多孔材料的发展、特点及其在改善中药挥发油稳定性的应用研究进行综述, 并探讨了影响多孔介质对中药挥发油吸附稳定性的研究策略, 以期对中药挥发油的稳定化控制与应用提供参考与借鉴。

**关键词:** 中药挥发油; 多孔材料; 介孔二氧化硅; 介孔碳; 金属有机框架

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## Research and application of porous materials adsorption technology to improve the stability of volatile oil of traditional Chinese medicine

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**Abstract:** As the main chemical component of aromatic traditional Chinese medicine (TCM), the volatile oil of TCM has significant pharmacological effects, such as antibacterial, anti-inflammatory, antioxidant and so on. However, TCM volatile oil is easy to volatilize and oxidize, which seriously limits its application. As a kind of grid structure material, porous material has the characteristics of high specific surface area, large pore volume, adjustable pore size, strong adsorption capacity and controllable surface chemical properties. It has been widely used in adsorption separation, biomedicine, industrial catalysis, wastewater treatment and other fields. In recent years, the use of porous materials to adsorb volatile oil has provided a new strategy and method for improving the stability of TCM volatile oils. At the same time, it can realize the solidification and stability of TCM volatile oils and the application of preparations. In this review, the development and characteristics of porous materials such as mesoporous silica, mesoporous carbon, mesoporous nano hydroxyapatite, porous metal organic framework, porous starch and their application in improving the stability of TCM volatile oils are summarized, and the research strategies affecting the adsorption stability of porous materials for TCM volatile oils are discussed, in order to provide reference for the stabilization control and application of TCM volatile oils.

**Key words:** volatile oil of traditional Chinese medicine; porous material; mesoporous silica; mesoporous carbon; metal-organic framework

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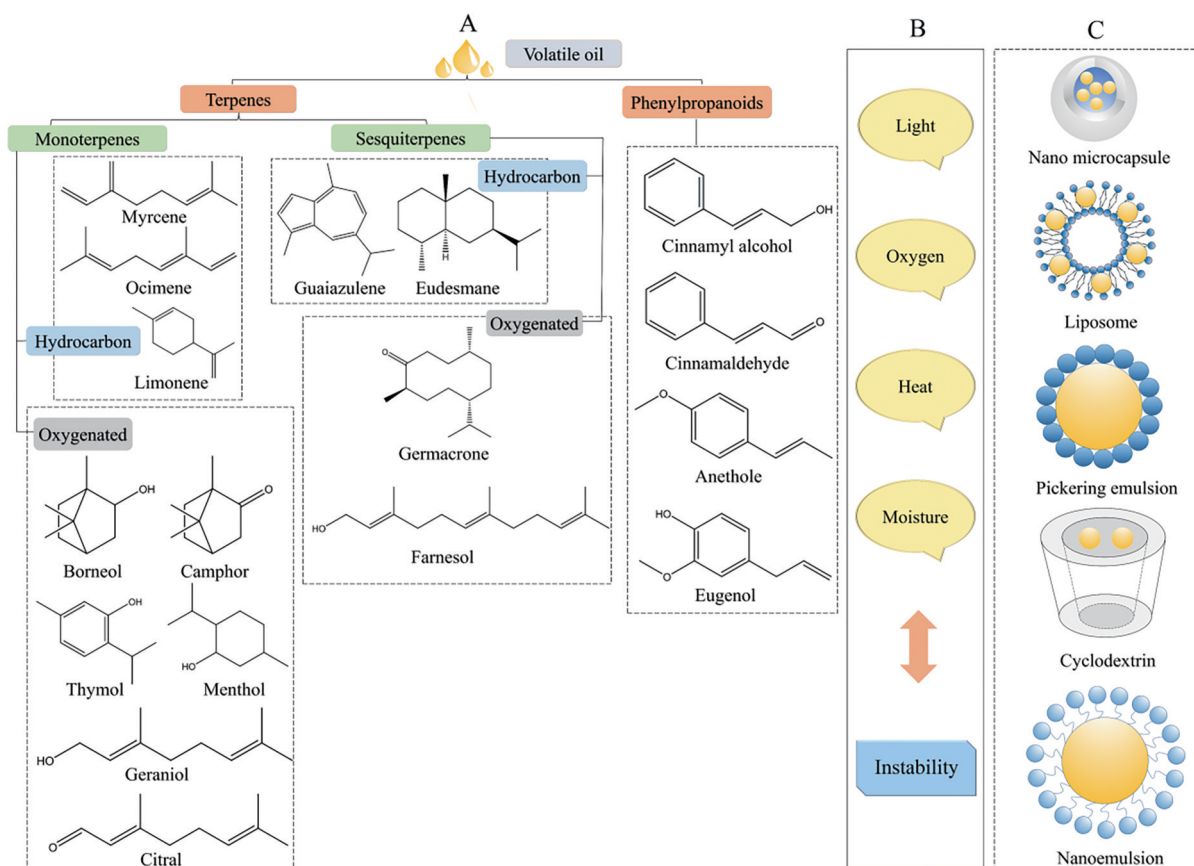
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中药挥发油作为芳香类中药的主要化学成分, 具有显著的药理活性, 广泛应用于中药制剂中, 具有重要的临床价值。然而中药挥发油有成分复杂、易挥发、易氧化变质等不稳定性问题, 限制了其在临床上的使用<sup>[1-3]</sup>。如何提高挥发油的稳定性一直是药剂学家关注的热点和难点。多孔介质吸附技术为改善中药挥发油的稳定性提供新的策略方法, 同时可实现中药挥发油的固体粉末化, 便于制剂应用。近年来多孔材料已成为吸附分离、生物医学、工业催化等领域的研究热点<sup>[4-6]</sup>。多孔介质吸附技术系主要利用多孔介质材料比表面积大、孔体积大及吸附能力强等特点<sup>[4-6]</sup>, 实现挥发油高效吸附, 以改善中药挥发油成分的挥发性, 从而控制挥发油的质量稳定, 提升含挥发油制剂的质量。本文对多孔介质材料的发展概况及其改善中药挥发油稳定性的应用研究进行综述, 并探讨了改善多孔吸附材料对中药挥发油吸附稳定性能的研究策略, 以期对中药挥发油的稳定化控制与制剂应用提供参考与借鉴。

### 1 中药挥发油的稳定性问题

中药挥发油又称精油, 是从芳香中药中提取的挥发性、具有强烈香味的化学成分, 具有显著的抗菌、抗

炎、抗氧化等药理活性, 被广泛应用于中药制剂中。如图1A所示, 中药挥发油主要活性成分为萜类及苯丙素类, 如单萜、倍半萜及含氧衍生物等成分<sup>[7]</sup>, 在常温下易挥发, 在光、热、湿及氧气下不稳定(图1B), 易发生氧化、异构化、环化或脱氢等化学反应<sup>[2,7,8]</sup>。Sebaaly等<sup>[9]</sup>发现挥发性成分丁香酚在室温且暗处下稳定, 在96 h后仍有80%的成分残留; 但暴露于紫外灯下的丁香酚浓度明显降低, 在96 h后仅剩2.9%。Tai等<sup>[10]</sup>探索了姜黄挥发油的热稳定性, 实验结果表明在加热温度为100 °C, 加热时间为8 h的条件下, 姜黄挥发性成分变化最为剧烈, 可能是某些热不稳定成分之间发生了构型转变所致。常见的改善中药挥发油稳定性的有效途径是对中药挥发油成分进行包合或包埋(图1C), 常用的包合技术方法有环糊精包合技术、纳米乳、微胶囊技术、Pickering乳化技术和脂质体纳米技术等<sup>[7,11,12]</sup>。尽管中药挥发油新型制剂技术的研究取得了一定进展, 但仍存在制备工艺复杂、载油量低等问题, 如环糊精包合技术对挥发油的分子大小或理化性质等具有特殊要求, 且需依赖比例较高的环糊精等辅料, 导致载油率相对较低<sup>[8]</sup>, 因此限制了此类技术在中药挥发油制剂中广泛应用。



**Figure 1** A: Structure of typical components in traditional Chinese medicine (TCM) volatile oils. B: Factors affecting the stability of TCM volatile oils. C: Nanoformulation strategy to improve the stability of TCM volatile oils

## 2 多孔材料的发展概况

近年来,许多学者将多孔材料应用到中药挥发油制剂领域中,利用其多孔结构吸附固化挥发油,实现中药挥发油的稳定控制。多孔材料是一种网格结构材料,由相互连接或封闭的孔组成,由于其物理或化学性质将客体元素限制在其外部或内部壁/孔内<sup>[4]</sup>。多孔材料主要是其有机物或无机物前体在模板剂的作用下,借助有机超分子/无机物的界面作用,形成具有一定结构和形貌的自组装材料,再经煅烧或化学处理去除模板剂而制得<sup>[13,14]</sup>。多孔材料凭借其大的比表面积和孔体积、可调节的孔径、吸附能力强及易于功能化的表面性质等特点,已在吸附分离、生物医学、工业催化、废水处理等领域中有较广泛的应用<sup>[4-6]</sup>。此外,多孔吸附材料的孔径大小、比表面积、孔体积和表面性质也是影响多孔材料吸附中药挥发油的重要因素,可通过调节这些特性来改善其吸附性能。

### 2.1 多孔材料的发展历程

多孔材料近年得到较大发展,尤其是纳米材料方面。如图2<sup>[15-26]</sup>所示,沸石分子筛(硅铝酸盐)作为微孔材料(孔径通常小于2 nm)代表,其人工合成源自20世纪40年代。Barrer<sup>[15]</sup>于1948年研究天然矿物在热的盐溶液中相态转变情况,首次合成了沸石分子筛。而金属多孔材料是20世纪80年代后期国际上迅速发展起来的,自Hoskins和Robson于1989年首次报道<sup>[16]</sup>以来,该微孔材料引起了广泛关注。1995年,Yaghi等<sup>[17]</sup>报道了一个由刚性有机配体均苯三甲酸与过渡金属Co合成的具有二维结构的配位化合物,称其为金属有

机框架(metal-organic frameworks, MOFs)。1999年,Li等<sup>[18]</sup>首次报道了以刚性有机配体对苯二甲酸和过渡金属Zn构筑的具有简单立方结构的三维金属有机骨架材料MOF-5,其骨架空旷度55%~61%,骨架结构可稳定至300℃。但微孔材料因孔径细小和孔径分布较宽等限制了其在大分子的吸附及催化领域的应用<sup>[14]</sup>。因此,多孔材料的研究也从微孔扩展到了介孔领域。

介孔材料分为硅系和非硅系两类,硅系介孔材料国内外研究较多,而非硅系介孔材料的研究起步相对较晚。90年代初,有序介孔材料作为一类新型纳米结构材料而迅速兴起<sup>[14]</sup>。1992年Mobil公司首次运用胶束软模板法开发了M41S系列介孔二氧化硅(mesoporous silica),如MCM-41(mobil composition of matter-41)、MCM-48、MCM-50,推动了硅系介孔材料的发展<sup>[19]</sup>。1998年,Zhao等<sup>[20]</sup>使用聚合物表面活性剂在强酸性(pH=1)体系中合成了一种新型介孔硅,将其命名为SBA-15(Santa Barbara amorphous-15),其高度有序、孔径大、比表面积高达800 m<sup>2</sup>·g<sup>-1</sup>。1995年,Antonelli等<sup>[21]</sup>报道了第一种稳定的非硅基介孔材料—介孔二氧化钛(mesoporous titanium dioxide),其平均孔径为3.2 nm,350℃焙烧后比表面积可达200 m<sup>2</sup>·g<sup>-1</sup>。而后又相继出现了有序介孔碳(mesoporous carbon)<sup>[22,23]</sup>、磷酸盐<sup>[24]</sup>等非硅系介孔材料。2001年,Vallet-Regi等<sup>[25]</sup>首次提出将介孔二氧化硅作为药物载体用于控制药物释放,从此介孔材料开始在医药领域引起广泛关注,尤其是介孔二氧化硅材料,凭借其孔径大小可调,表面易于功能化修饰及生物相容性好等特点,被广泛应用于药物吸

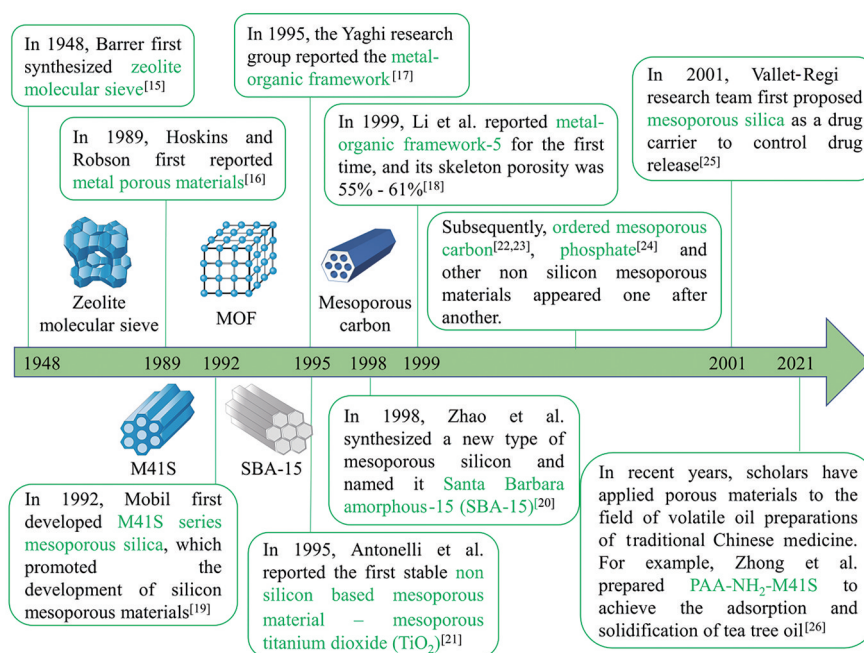


Figure 2 Development of porous materials. PAA: Polyacrylic acid

附、分离、递送等研究领域。近年来,许多学者将介孔材料应用到中药挥发油制剂领域中,利用其多孔结构吸附固化挥发油,实现中药挥发油的稳定控制<sup>[26]</sup>。

## 2.2 多孔材料的分类

### 2.2.1 按孔径大小分类

根据国际纯粹与应用化学联合会 (International Union of Pure and Applied Chemistry) 的定义<sup>[27]</sup>,按孔径大小将多孔材料分为微孔、介孔、大孔材料 (表 1)。微孔材料的代表有沸石分子筛,气凝胶,以及磷酸盐、硫酸盐、砷酸盐等类沸石。该类材料具有良好的吸附能力、较高的热稳定性;但孔径细小,且孔径分布较宽<sup>[14]</sup>。介孔材料如介孔二氧化硅、介孔碳、介孔纳米羟基磷灰石 (hydroxyapatite, HAp) 等比表面积高、孔体积大、易于表面功能化,可经优化处理得到较好的热稳定性和一定的水热稳定性<sup>[26]</sup>。早期的大孔材料内部结构不规则,孔径较宽,但强度不高,制备所需时间较长且成本较高;后期出现的三维有序材料如大孔二氧化硅等孔道整齐有序,孔径均一<sup>[28]</sup>。

### 2.2.2 按化学组成分类

根据化学组成分类,多孔材料可分为硅基多孔材料、非硅基多孔材料;前者又分为纯硅类 (如介孔二氧化硅系列) 和掺杂其他元素类 (如矿物硅酸盐类),后者主要包括介孔碳、介孔磷酸盐、介孔金属氧化物、硫化物及有机多孔淀粉 (porous starch) 等<sup>[29]</sup> (图 3)。

## 3 多孔吸附材料改善中药挥发油稳定性的研究概况

本文重点围绕介孔二氧化硅、介孔碳、介孔纳米 HAp、MOFs、多孔淀粉等多孔材料,论述其在中药挥发

油的研究应用情况。多孔材料对中药挥发油中的吸附应用实例见表 2<sup>[30-49]</sup>。

## 3.1 介孔二氧化硅改善中药挥发油稳定性的应用研究

介孔二氧化硅是指孔径在 2~50 nm 的含硅基的一类介孔材料,具有以下特性:① 孔隙网络有序,大小均匀,能精细控制载药和释放;② 孔隙体积大,载药空间大;③ 高比表面积,药物吸附能力强;④ 含硅醇的表面可功能化,可更好地控制药物的装载和释放<sup>[40,50]</sup>,同时介孔二氧化硅材料具有出色的结构稳定性,这些特点使其在吸附分离、药物递送、生物医学等领域中具有极其重要的作用。但介孔二氧化硅也存在如体内降解速度慢、存在溶血作用等不足<sup>[51]</sup>。

Zhong 等<sup>[26]</sup>用聚丙烯酸 (polyacrylic acid, PAA) 对胺化的介孔二氧化硅 (aminated mesoporous silica, NH<sub>2</sub>-M41S) 进行改性,研究其对茶树油 (tea tree oil, TTO) 的影响。结果所示 TTO 在 2 h 内完全释放,而 TTO/M41S、TTO/PAA-NH<sub>2</sub>-M41S 分别在 2.8、7 h 时累积释放率达到 50%,说明以介孔二氧化硅为载体可减少 TTO 的挥发,可能是孔隙的空间位阻和硅醇基团与 TTO 间形成氢键所致;经 PAA 改性后的 M41S 更有效降低了 TTO 的释放,因为 PAA 降低了 M41S 的比表面积和孔体积,限制了 TTO 的挥发。Zhong 等<sup>[26]</sup>还研究了纯 TTO 和复合载体 TTO/PAA-NH<sub>2</sub>-M41S 的抗菌性能。结果显示,复合载体的细菌抑制区直径明显大于纯 TTO 的直径,表明使用介孔二氧化硅作为载体可有

Table 1 Classification of porous materials

Classification	Pore size/nm	Representative material
Microporous	< 2	Zeolite molecular sieve; phosphate, arsenate, sulfate and other zeolite-like
Mesoporous	2-50	Mesoporous alumina; mesoporous carbon; mesoporous phosphate; mesoporous silica
Macroporous	> 50	Porous glass; three-dimensional ordered macroporous material

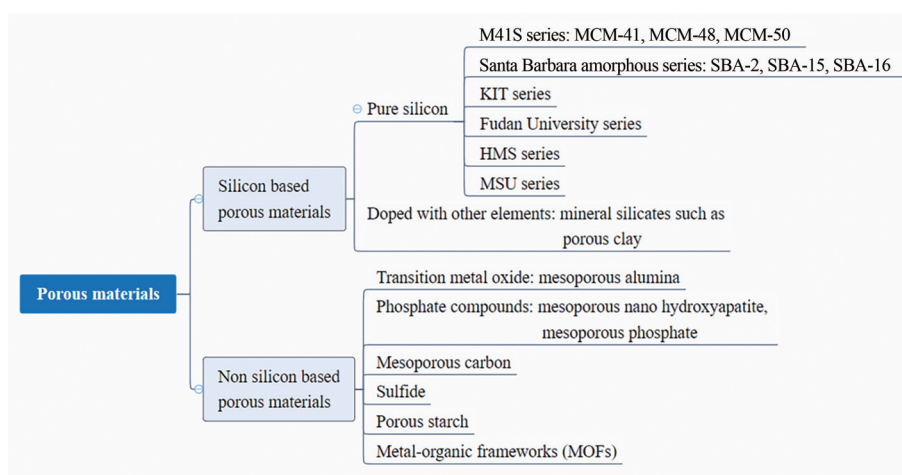


Figure 3 Classification of porous materials by chemical composition

**Table 2** Application examples of porous materials adsorbing TCM volatile oils. MOFs: Metal-organic frameworks; MCM-41: Mobil composition of matter-41; SBA-15: Santa Barbara amorphous-15

Name of volatile oil	Porous material	Pore size /nm	Specific surface area /m <sup>2</sup> ·g <sup>-1</sup>	Pore volume /cm <sup>3</sup> ·g <sup>-1</sup>	Achieved result
Clove oil, zedoary turmeric oil <sup>[30]</sup>	Mesoporous carbon	-	-	-	Increased dissolution of volatile components and improved thermal stability
Lavender essential oil and basil essential oil <sup>[31]</sup>	Hydroxyapatite	17.48	98.45	0.38	Significantly improved the antibacterial effect
<i>D</i> -Limonene <sup>[32]</sup>	$\gamma$ -Cyclodextrin MOF	-	-	-	Inhibited the volatilization and improved the stability of <i>D</i> -limonene
Fragrance substance <sup>[33]</sup>	Zirconium based MOFs	-	-	-	Slowed down the release of fragrance substances
Tea tree oil <sup>[34]</sup>	M41S	3.09	1 026	0.612	Effectively delayed the evaporation and improved the long-term antibacterial performance of tea tree oil
Tea tree oil <sup>[35]</sup>	MCM-41	3.2	640	0.496	Slowed down the release of volatile oil, so as to improve the antibacterial activity
Pepper fragrant essential oil <sup>[36]</sup>	MCM-41	-	-	-	Showed sustained-release effect and enhanced antibacterial activity
Essential oil components <sup>[37]</sup>	MCM-41	-	-	-	Enhanced the antibacterial property
<i>Thymus eriocalyx</i> and <i>Thymus kotschyanus</i> essential oils <sup>[38]</sup>	MCM-41	-	-	-	Improved the stability and durability of essential oil, enhanced the effect of mite control
Tea tree oil <sup>[39]</sup>	MCM-41	3.068	848.018	0.532	Slowed down the evaporation rate, prolonged and enhanced the antibacterial effect
Tea tree oil <sup>[40]</sup>	Mesoporous silica	3.09	1 026	0.612	Slowed down the release and had better antibacterial properties
<i>Thyme</i> essential oil <sup>[41]</sup>	SBA-15, MCM-41	-	-	-	Delayed release and improved performance
Volatile oil of <i>Bupleuri radix</i> and <i>Forsythiae fructus</i> <sup>[42]</sup>	Mesoporous silica sylvesia 350FCP	-	-	-	Had the advantages of large drug loading, improved the thermal stability and mechanical stability of volatile oil
Volatile oil of <i>Citri Reticulatae</i>	Mesoporous silica 350FCP	18.176	281.975	1.281	Slowed down the release of volatile oil
<i>Pericarpium and Citri Reticulatae</i>					
<i>Pericarpium Viride</i> <sup>[43]</sup>					
Clove essential oil <sup>[44]</sup>	Mesoporous silica nanoparticles	-	-	-	Sustained release and good antibacterial activity
Patchouli essential oil <sup>[45]</sup>	Mesoporous silica nanoparticles	-	-	-	Sustained release, good long-term antibacterial effect on <i>Staphylococcus aureus</i>
Cinnamon oil <sup>[46]</sup>	Mesoporous silica nanoparticles	-	-	-	Enhanced antibacterial effect
Orange oil and <i>Thyme</i> oil <sup>[47]</sup>	Porous halloysite, octadecyl modified montmorillonite	-	-	-	Increased the spacing between porous clay layers, showed higher adsorption rate and better interaction
Olive oil <sup>[48]</sup>	Porous starch	-	-	-	Improved the oxidation stability of olive oil and significantly prolonged the shelf life of olive oil
Clove essential oil <sup>[49]</sup>	Three dimensional nanonetwork porous starch-based material	-	-	-	Significantly prolonged the duration of antibacterial activity, and had higher antibacterial effect

效减少TTO挥发,从而维持抗菌效果。

Bernardos等<sup>[37]</sup>研究了负载精油的介孔二氧化硅对黑曲霉的体外抗真菌活性。研究表明,经MCM-41包被的香芹酚和百里香酚在30天后的抑菌率是纯精油成分的2倍、是环糊精包合物的3倍,表明介孔二氧化硅材料包被后的精油成分具有更好的稳定性,长期储存后仍保持较强的抗真菌活性。

### 3.2 介孔碳改善中药挥发油稳定性的应用研究

介孔碳是指在孔径2~50 nm内具有窄或宽的孔隙分布的一类新型非硅基介孔材料<sup>[52,53]</sup>,可通过模板法、水热合成法、溶胶-凝胶法等方法制备<sup>[53,54]</sup>。介孔碳材料具有均匀可调的孔径、高比表面积、大孔体积、有序的孔结构,良好的导电性、热稳定性等特点<sup>[55,56]</sup>,凭借其高吸附效率和良好的生物相容性,在药物输送系统中得以发展<sup>[53]</sup>。介孔碳对有机物的吸附能力远优于活性炭,且能改善微孔材料吸附后难脱附的现象<sup>[30]</sup>。此外,介孔碳材料在大生物分子的吸附和分离、空气净化领域也被广泛应用。然而,介孔碳材料的疏水性和惰性限制了其在吸附领域的应用,可通过表面修饰改善其性能,如引入极性官能团羧基等<sup>[53]</sup>。

Yan等<sup>[30]</sup>考察不同比例介孔碳吸附对丁香油和莪术油中的指标成分的影响。研究表明,挥发性成分的吸附率随介孔碳用量的增加而提高,当介孔碳与挥发油的质量比达到1:1时,吸附率可达90%以上。经介孔碳粉末吸附后的粉体流动性好,挥发油的溶出度增加,受热稳定性也有所提高,在40、60℃条件下的挥发油指标成分的损失率明显降低,表明介孔碳吸附固化挥发油可减少其损失,改善挥发油易挥发和不稳定的性质。

### 3.3 介孔纳米HAp改善中药挥发油稳定性的应用研究

HAp是人体骨骼的主要组成部分,是一种钙和磷酸盐的化合物<sup>[31,57]</sup>,具有生物相容性,是医药领域最常用的材料之一<sup>[57]</sup>。HAp具有天然孔道结构所形成的微孔,有较强的表面吸附性、离子交换性及良好的热稳定性<sup>[58,59]</sup>,常作为药物载体材料<sup>[57]</sup>,在吸附、催化、医学、分离、生物材料等领域具较好的发展前景<sup>[31,57]</sup>。然而,HAp材料的机械性能较差,存在脆性大、生理环境下抗疲劳与抗破坏强度低等缺陷,将HAp制成分级多孔或与其他物质杂化制成复合材料是目前主要的研究方向<sup>[58]</sup>。

Predoi等<sup>[31]</sup>制备了HAp,所得粉末分别与薰衣草精油、罗勒精油混合,再压制成直径为6 mm的球团。负载精油后的纳米粒分布变得不均匀,孔隙率明显增加,且比表面积和孔体积都增大。抑菌实验结果表明,HAp

纳米粒对革兰阳性菌和革兰阴性菌均无抑菌活性;相比纯精油,HAp负载薰衣草精油(hydroxyapatite-lavender essential oil, HAp-LEO)对所测菌株展现出更强的生长抑制作用。Predoi等<sup>[57]</sup>还发现,负载精油后的HAp纳米粒的粒径比纯HAp小;与单独使用HAp相比,经薰衣草精油包覆的HAp的抗菌效果显著提高,表明HAp纳米粒可作为薰衣草精油的载体,发挥抗菌性能。

### 3.4 MOFs材料改善中药挥发油稳定性的应用研究

MOFs是一种由有机配体和金属离子/金属簇通过配位键组成的二维或三维网络晶体材料<sup>[16,60]</sup>。相比于其他传统吸附剂,MOFs具有高度多孔性和结晶性、比表面积大、吸附容量大、孔道可调节、化学可修饰性及结构组成多样性等特点<sup>[16]</sup>。然而,MOFs在生理条件下不稳定,易分解或使药物过早释放,主要原因是生理环境中的各种分子与金属离子相互作用,导致框架坍塌或降解<sup>[16]</sup>,可通过官能团修饰改善其性能<sup>[33]</sup>。

由于其高比表面积和有序的多孔结构,MOFs在气体吸附和分离、催化、光电、传感、能量储存和生物医学等方面广泛应用<sup>[61]</sup>。Zhou等<sup>[32]</sup>将D-柠檬烯(D-limonene, D-Lim)加载到 $\gamma$ -环糊精金属有机框架( $\gamma$ -cyclodextrin metal-organic framework,  $\gamma$ -CD-MOF)材料上,结果表明,装载后的D-Lim的溶解度增加。热重分析结果(thermogravimetry analysis, TGA)表明,D-Lim在119℃已完全挥发,而装载后的D-Lim在129℃才开始分解,说明 $\gamma$ -CD-MOF包封抑制了D-Lim的挥发,提高其稳定性。Liu等<sup>[33]</sup>制备了铅基MOFs材料,评估MOFs作为纳米载体封装和控释挥发性芳香物质的能力。TGA结果表明,非极性MOFs的分解温度达500℃,极性羟基官能化MOFs的分解温度可达300℃,表明其热稳定性较高。释放曲线表明,室温下的芳香物质丙酸乙酯在2天内迅速释放且释放量达到90%以上,而加载了MOFs的芳香物质呈持续释放趋势,在2天内的释放量低于50%,表明芳香物质经MOFs装载后可起到缓释作用。

### 3.5 多孔淀粉改善中药挥发油稳定性的应用研究

多孔淀粉是一种新型的变性淀粉,其颗粒表面不规则且多孔<sup>[48,62]</sup>,能吸附其本身质量70%~80%的液体而形成固体粉末状<sup>[63]</sup>。与天然淀粉相比,多孔淀粉因其大的比表面积而具有很强的吸附能力,且其机械强度高,耐压性更强<sup>[49]</sup>,具有良好的生物相容性和可降解性,可作为绿色高效的吸附剂<sup>[49,63]</sup>,被广泛用于医药、食品、日用化工等行业。但多孔淀粉孔径较小、吸附缺乏选择性,稳定性差,如单一的多孔淀粉作为壁材时制备的微胶囊并不稳定,可通过两种或两种以上壁

材复合使用来改善稳定性<sup>[49,64]</sup>。

Sun 等<sup>[62]</sup>利用多孔淀粉来吸附茴香精油 (fennel essential oil, FEO), 并将其制成微胶囊。体外释放研究表明微胶囊中的 FEO 单日释放速率逐渐降低, 表明 FEO 微胶囊具有良好的缓释能力, 从而维持较长时间的抗菌活性, 将其应用于食品中可在较长时间内保持肉制品的质量。Fang 等<sup>[49]</sup>利用三维纳米网络多孔淀粉基材料 (three dimensional nanonetwork porous starch-based material, 3D-NPS) 负载丁香精油 (clove essential oil, CEO)。结果表明, 负载 CEO 的 3D-NPS 最大封装效率达到 86.7%, 且具有更强的热处理稳定性和抗压能力。与纯 CEO 对比, 负载 CEO 的 3D-NPS 复合物的抗菌活性持续时间明显延长, 且抑菌效果明显高于纯 CEO。

#### 4 改善多孔材料吸附中药挥发油稳定性的研究策略

##### 4.1 调节多孔材料结构特性并提高多孔材料的吸附性能

多孔材料按照孔径的大小分为微孔、介孔、大孔材料。多孔材料的孔径、比表面积和孔体积大小对其吸附性能有明显影响。如 Zhong 等<sup>[26]</sup>制备的 M41S、NH<sub>2</sub>-M41S、PAA-NH<sub>2</sub>-M41S-2 的平均孔径分别为 2.896、2.770、1.542 nm, 胺化前后的比表面积分别为 854.362、589.214 m<sup>2</sup>·g<sup>-1</sup>, 孔体积从 0.587 降至 0.338 cm<sup>3</sup>·g<sup>-1</sup>, 说明胺化改性和 PAA 都导致了孔径、比表面积和孔体积的减小, 而 PAA-NH<sub>2</sub>-M41S 吸附的茶树油释放时间延长, 且随着 PAA 分子质量的提高, 持续释放时间延长, 原因是 PAA 降低了介孔二氧化硅的孔径、比表面积和孔体积, 而限制了 TTO 的挥发。本课题组前期制备了海绵状介孔二氧化硅, 其比表面积和孔体积分别为 815.728 m<sup>2</sup>·g<sup>-1</sup> 和 1.804 cm<sup>3</sup>·g<sup>-1</sup>, 对中药挥发油的载油率高达 76.3%, 且负载后挥发油的热稳定性和释放行为得到显著改善。可见多孔材料的孔径大小、比表面积和孔体积是影响其对挥发油吸附稳定的重要因素。通过优化多孔材料的制备方法, 调节其多孔结构特性, 可提高多孔材料对中药挥发油的吸附性能。

##### 4.2 优化多孔材料的表面性质, 提升多孔材料的吸附作用

多孔材料具有易于功能化的表面性质, 以便更好地控制药物的装载和释放。如 Chen 等<sup>[35]</sup>将聚乙烯亚胺 (polyethyleneimine, PEI) 装载到 MCM-41 上, 装载后的比表面积和孔体积较原始 MCM-41 有所下降。由于 PEI 进入到介孔中, 经改性后的复合材料对茶树油的加载量有所降低。复合材料 TTO/PEI-MCM-41 在 12 h 内的茶树油累积释放率明显小于 TTO/MCM-41,

展现出较好的缓释性能。本课题组运用 1,2-双三甲氧基硅基乙烷与正硅酸乙酯共缩聚模板法制备了有机改性修饰的介孔二氧化硅, 考察了其对于中药薄荷挥发油吸附性能, 结果也发现, 相比无机介孔二氧化硅, 有机改性修饰介孔二氧化硅负载的薄荷油, 热失重速率显著变慢, 延缓了薄荷挥发油的稳定性。因此, 通过化学基团的改性修饰来优化多孔材料的表面性质, 可提升多孔材料对中药挥发油的吸附稳定性。

#### 5 总结与展望

多孔介质吸附固化技术为改善中药挥发油的稳定性提供新的方法。多孔材料如介孔二氧化硅、介孔碳、MOFs 等制备简单、热稳定性高, 同时具有高比表面积和孔体积、孔径可调、吸附能力强、表面化学性能可控等特点, 用其吸附固化挥发油为改善中药挥发油的稳定性提供新的载体, 同时可实现中药挥发油的固体粉末化, 便于制剂加工应用。然而, 多孔材料的孔径大小、比表面积、表面特性及结构的稳定性是影响其对挥发油吸附性能的关键因素。通过优化制备工艺, 调节多孔结构的结构特性与表面化学性质, 提高多孔材料对中药挥发油的吸附性能, 将进一步拓展多孔吸附材料在改善中药挥发油稳定性方面的应用前景。

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