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# Supercritical carbon dioxide systems for sustainable and efficient dissolution of solutes: a review

Xing Kang<sup>1</sup> · Liuhaio Mao<sup>1</sup> · Jinwen Shi<sup>1</sup>  · Yanbing Liu<sup>1</sup> · Binjiang Zhai<sup>1</sup> · Jun Xu<sup>2</sup> · Yuzhou Jiang<sup>1,3</sup> · Eric Lichtfouse<sup>1</sup> · Hui Jin<sup>1</sup> · Liejin Guo<sup>1</sup>

## Abstract

Green chemistry aims at replacing toxic solvents by safer solvents such as supercritical carbon dioxide (scCO<sub>2</sub>), which displays zero surface tension, outstanding transport properties, high diffusivity, and tuned solubilization by changing the pressure and temperature, or adding cosolvents. Nonetheless, the practical application of scCO<sub>2</sub>-based technologies under supercritical conditions requires sophisticated systems for optimal operation. Here, we review scCO<sub>2</sub>-based systems with focus on dyeing, extraction, chromatographic, and cleaning systems. All scCO<sub>2</sub>-based systems consist of a CO<sub>2</sub> supply and pump part, a cosolvent providing part, and a parameters controlling part, yet there are different reaction vessels depending on solute types and practical functions. Developing more normalized, intelligentized, and durable scCO<sub>2</sub>-based systems should render the scCO<sub>2</sub>-based technologies be more economic, controllable, flexible, and suitable for wider applications.

**Keywords** Apparatus · CO<sub>2</sub> · Equipment · Green solvent · Reactor · Supercritical fluid

## Introduction

Since the chemist Anastas (1999) introduced the concept of “green chemistry” in 1990s, avoiding the utilization of toxic reagents and solvents has become the tendency in the manufacture and chemical industries (Cao and Su 2021). Toxic solvents have been widely used in industrial processes despite the high risk of contaminating the environment (Anastas and Eghbali 2010; Aravindhnan et al. 2017). However, the solvents cannot be absolutely avoided due to their vital role for dissolving components, promoting mass and heat transfer, and accelerating the reaction process (Mohammad and Inamuddin 2012; Cheng et al. 2023). Accordingly,

there is an urgent need for more environmentally friendly and efficient solvents (Pacheco-Fernández and Pino 2019).

Supercritical carbon dioxide (scCO<sub>2</sub>) as a sustainable and efficient solvent with mild critical temperature of 304.1 K and critical pressure of 7.4 MPa has attracted increasing attention in recent years (Liu et al. 2006; Qi et al. 2018; Ramsey et al. 2009). ScCO<sub>2</sub> with low viscosity, zero surface tension, high gas-like diffusivity, and high liquid-like density has becoming an attractive solvent that can be widely used in various fields (Bai et al. 2019; Lebedev et al. 2015). Moreover, scCO<sub>2</sub> can be completely miscible with the gas solutes, while the solubility of the liquid and solid solutes in scCO<sub>2</sub> can be adjusted by flexibly varying the temperature and pressure as well as adding cosolvents during the scCO<sub>2</sub>-assisted reaction process (Chauvet et al. 2017; Kang et al. 2020). The use of scCO<sub>2</sub> as the solvent also has the advantages of easy recompression, complete separation with the solutes by simply depressurization, and recycled utilization of CO<sub>2</sub> (Machado et al. 2013; Sihvonen et al. 1999). ScCO<sub>2</sub> has been widely applied for dissolving various types of solutes, such as dyes, target solutes in other solvents, component solutes to be separated or purified, and contaminants to be removed, among which especially for non-polar solutes, based on different scCO<sub>2</sub>-based technologies, i.e., dyeing technology, extraction technology, chromatography technology, and

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cleaning technology, respectively (Aslanidou et al. 2013; Friedrich and Pryde 1984; Rezaei and Temelli 2000). It is also worth noting that scCO<sub>2</sub>-based technologies are limited since scCO<sub>2</sub> lacks polarity and capacity to form specific solvent–solute interaction, and several studies have found that the addition of a small amount of proper cosolvent can effectively improve its solvent power for part of non-polar solutes (Li et al. 2003; Ting et al. 1993; Güçlü-Üstündağ et al. 2005; Zulkaffi et al. 2014; Patil et al. 2018).

Recent reviews on scCO<sub>2</sub>-based technologies mainly focus on the reactions that performed assisted by scCO<sub>2</sub> as the solvent. Gonzalez et al. (2014) comprehensively presented the perspectives of scCO<sub>2</sub>/green solvent biphasic systems to offer a good insight into the practical usages and potential applications of the scCO<sub>2</sub>/green solvent biphasic systems. Abou et al. (2018) highlighted the great role of scCO<sub>2</sub>-based technology in textile dyeing processes, which shows a detailed introduction about scCO<sub>2</sub>-assisted dyeing applications. Moreover, Sharif et al. (2014) introduced the common experimental designs using in the supercritical fluid extraction process and further analyzed the influential factors. Speybrouck et al. (2016) systematically summarized the advantages of using scCO<sub>2</sub> as the mobile phase, such as short equilibration time, high flow rate, and very low solvent consumption, for analytical and preparative chiral supercritical fluid chromatography. Additionally, Meziani et al. (2017) comprehensively elaborated novel scCO<sub>2</sub>-assisted cleaning applications in the semiconductor cleaning process and introduced the recent advances of the scCO<sub>2</sub>-assisted cleaning applications in the emerging technologies. All of these offer a valuable view in the aspects of scCO<sub>2</sub> as a green solvent for flexible and efficient dissolution of various types of solutes. However, it is worth noting that the practical application of scCO<sub>2</sub>-based technologies under supercritical reaction conditions requires sophisticated systems for optimal operation. Although many different types of scCO<sub>2</sub>-based systems have been built, there is actually no reported review detailing various scCO<sub>2</sub>-based systems used for different scCO<sub>2</sub>-based applications.

Herein, compared to most reviews that focused on the reactions that performed assisted by scCO<sub>2</sub> as the solvent, this review summarizes the current research status of the scCO<sub>2</sub>-based systems for flexible and efficient dissolution of different types of solutes, such as dyes, target solutes in other solvents, component solutes to be separated or purified, and contaminants to be removed, based on different scCO<sub>2</sub>-based technologies and related systems, i.e., dyeing system, extraction system, chromatograph system, and cleaning system. Additionally, this review also introduces the similarity and difference among the systems which matched with different practical production requirements in each application, and further successively points out the perspectives and valuable directions for future development in both fundamental

research and commercial applications of the scCO<sub>2</sub>-based systems. The outline of this review is shown in Fig. 1.

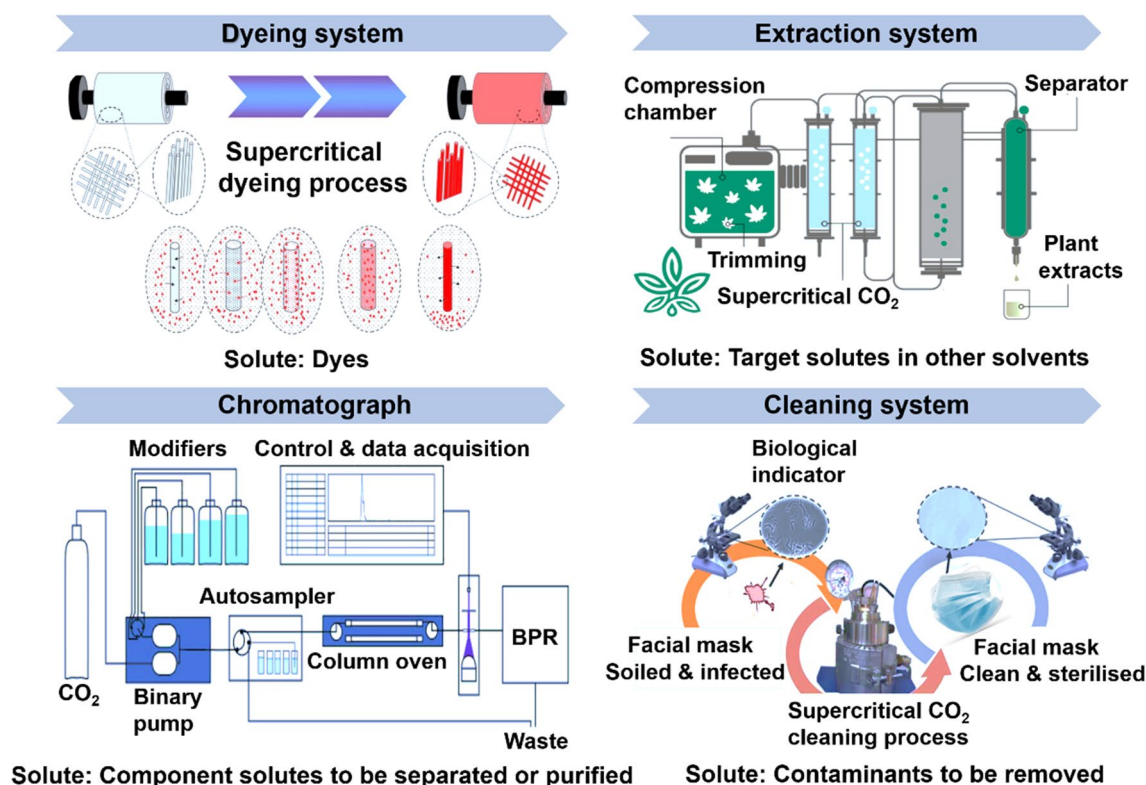
## Dyeing systems

The traditional printing and dyeing technology are mainly based on water as the solvent, which has the disadvantages of water consumption, energy consumption, and environmental pollution (Banchero 2013). As a consequence, Saus et al. (1993) invented the supercritical fluid dyeing technology. The supercritical fluid dyeing technology has shown excellent characteristics in overcoming the waste of water resources and serious waste pollution, and the most prominent supercritical fluid used for supercritical fluid dyeing is scCO<sub>2</sub> (Abou et al. 2015; Banchero 2013; Jaxel et al. 2020; Kazarian et al. 1997). ScCO<sub>2</sub> shows extremely high solubility and affinity of dyes; as a result, it could be used as medium to carry dyes to dye the fabrics. After dyeing, CO<sub>2</sub> and the unused dyes will be separated and recycled, which avoided the pollution at the source (Abou et al. 2018a, 2020; Banchero 2020).

Moreover, the scCO<sub>2</sub> dyeing technology does not have the washing and drying process that existed in the traditional dyeing technology, and not need to add dispersant, leveling agent, retarder, and other auxiliary agents during the dyeing process, which not only improves the production efficiency, but also reduces energy consumption, thus improving the economic efficiency (Abou et al. 2021; Agrawal 2015; Goñi et al. 2021). Therefore, developing the application and corresponding systems of scCO<sub>2</sub> dyeing technology will inject vitality into the printing and dyeing industry. The critical factors of scCO<sub>2</sub> dyeing systems are reasonable design of the high-pressure dyeing vessel that can satisfy the dye homogeneously dispersed and dissolved in scCO<sub>2</sub>, and then uniformly absorbed and diffused onto the fabric to realize the dyeing requirements. Meanwhile, separators should be designed for removing excess dye and residue. Actually, there are two types of scCO<sub>2</sub> dyeing methods, namely static dyeing and dynamic dyeing. The systems used in the above two scCO<sub>2</sub> dyeing methods are generally divided into static dyeing system, dynamic beam dyeing system, and dynamic jig dyeing system, respectively, which will be summarized and reviewed separately in the following.

### Static dyeing system

Static scCO<sub>2</sub> dyeing systems are typically applied in laboratory-scale scCO<sub>2</sub> dyeing process. Static scCO<sub>2</sub> dyeing systems are simply composed of CO<sub>2</sub> supply part, pressure- and temperature-controlling part, high-pressure dyeing vessel, and separator. In the traditional static scCO<sub>2</sub> dyeing system, the fabric, dye, and cosolvent are usually placed together



**Fig. 1** Sustainable-solvent-supercritical carbon dioxide (scCO<sub>2</sub>)-based systems for flexible and efficient dissolution of solutes. This report reviews scCO<sub>2</sub>-based systems for sustainable and efficient dissolution

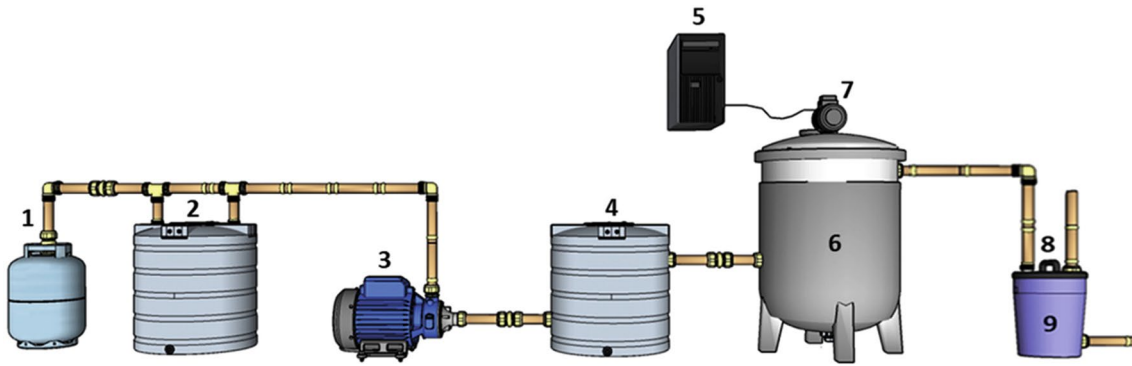
of different types of solutes, based on different scCO<sub>2</sub>-based technologies and associated systems, i.e., dyeing system, extraction system, chromatograph, and cleaning system. BPR: backpressure regulator

into the dyeing vessel, and then, CO<sub>2</sub> will be injected by the high-pressure pump. By adjusting the temperature and pressure to achieve the scCO<sub>2</sub> dyeing conditions, the dye will be continuously dissolved and diffused onto the fabric to complete the dyeing process. The core of the traditional scCO<sub>2</sub> dyeing system is the agitation device for promoting the movement of the dyeing solution in order to enhance the dyeing uniformity.

The typical static scCO<sub>2</sub> dyeing system is shown in Fig. 2 (Penthala et al. 2019). Here, the fabric, dye, and cosolvent are usually placed together into the dyeing vessel, and then, CO<sub>2</sub> will be injected by the high-pressure pump. By adjusting the temperature and pressure to achieve the scCO<sub>2</sub> dyeing conditions, the dye will be continuously dissolved and diffused onto the fabric to complete the dyeing process. The dyeing vessel usually equips with an agitation device to promote the movement of the dyeing solution in order to enhance the uniformity. After the reaction, the excess dye will be collected into the residual dye trap and CO<sub>2</sub> will also be recycled. Moreover, horizontal stirring of the fabric can overcome the influence of gravity during the dyeing process than the vertical stirring and thus further improve the color presentation uniformity; also, the small volume and easy

operation of the systems are also important factors for the practical applications of the scCO<sub>2</sub> dyeing systems. Aiming at the issue, Mo et al. (2020) designed an integrated static scCO<sub>2</sub> desizing system (Fig. S1), where the high-pressure autoclave is firstly pre-cooled down and then the fabric will be put in the autoclave. Subsequently, the autoclave is heated by the oil bath until it reached the target temperature and stirred continuously until realizing the dyeing process. Finally, the cooling water circulation will be turned on until the pressure of the autoclave decreases to the atmosphere pressure. Compared with the traditional static scCO<sub>2</sub> dyeing system, this system is equipped with an integrated heating and cooling tube, which can control the temperature and pressure more accurately. There are also two Z-shaped stirring shafts at both ends of the autoclave, and therefore, it is more conducive to promote the movement of dyeing solution than the vertical stirring and thus to make the dyeing process more homogeneous and efficiency.

The static scCO<sub>2</sub> dyeing system has been widely used in laboratory-scale dyeing experiments to study the effect of parameters, such as temperature, pressure, and time, on the dyeing of different fabrics during the scCO<sub>2</sub> dyeing process. However, due to the absence of fluid circulation during the



**Fig. 2** Typical static supercritical carbon dioxide (scCO<sub>2</sub>) dyeing system: 1. CO<sub>2</sub> cylinder, 2. circulated cooling bath, 3. high-pressure pump, 4. heating bath, 5. temperature controller, 6. dyeing vessel, 7. stirrer, 8. pressure regulator, and 9. separator. The fabric, dye, and cosolvent are usually placed together into the dyeing vessel, and then,

CO<sub>2</sub> will be injected by the high-pressure pump. The dye will be continuously dissolved and diffused onto the fabric to complete the dyeing process. Reproduced with permission of Elsevier from Penthala et al. (2019)

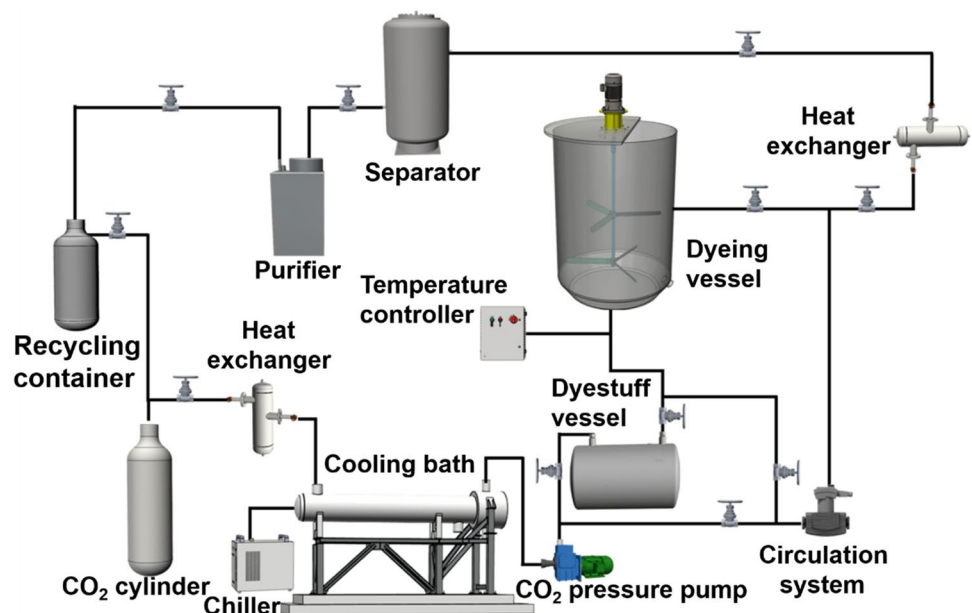
static scCO<sub>2</sub> dyeing process, the diffusion rate of dyeing solution and the dyeing efficiency is poor, even if the stirring device is used. Therefore, scientists have developed the dynamic scCO<sub>2</sub> dyeing technology, detailed in the next section.

### Dynamic dyeing system

Static scCO<sub>2</sub> dyeing system is lack of dyeing fluid circulation resulting in limited diffusion rate of dyeing solution and poor dyeing efficiency, even if the stirring device is used. Aiming at the issue, dyeing solution circulation device is designed in dynamic scCO<sub>2</sub> dyeing system for continuously circulating the dye between the dyeing vessel and the dyestuff vessel, ensuring that the dye enters the high-pressure

dyeing vessel with a saturated state. The continuous circulation of dyeing solution can strengthen the mass transfer process, thus improving the dyeing efficiency. Compared with the static scCO<sub>2</sub> dyeing system, the dynamic scCO<sub>2</sub> dyeing system equips with a dyeing solution circulation device (Fig. 3) (Penthala et al. 2020). During the dynamic scCO<sub>2</sub> dyeing process, the dispersed solid dye is packed into the dyestuff vessel and dissolved by scCO<sub>2</sub> and then circulated by the syringe pump passing through the filter into the dyeing vessel. The dyeing solution circulation can continuously circulate the dye between the dyeing vessel and the dyestuff vessel, ensuring that the dye enters the high-pressure dyeing vessel with a saturated state. The continuous circulation of dyeing solution strengthens the mass transfer process, thus improving the dyeing efficiency.

**Fig. 3** Dynamic supercritical carbon dioxide (scCO<sub>2</sub>) dyeing system. During the dynamic scCO<sub>2</sub> dyeing process, the dispersed solid dye will be packed into the dyestuff vessel and dissolved by scCO<sub>2</sub> and then circulated by the syringe pump passing through the filter into the dyeing vessel. The dyeing solution circulation can continuously circulate the dye between the dyeing vessel and the dyestuff vessel, ensuring that the dye enters the high-pressure dyeing vessel with a saturated state. Reproduced with permission of Elsevier from Penthala et al. (2020)





According to whether the fabric has reciprocating motion in the dyeing vessel, dynamic  $\text{scCO}_2$  dyeing systems can be divided into two types, i.e.,  $\text{scCO}_2$  beam dyeing system and  $\text{scCO}_2$  jig dyeing system, which will be introduced separately in the following.

### Dynamic beam dyeing system

The dynamic  $\text{scCO}_2$  beam dyeing system is one of the most widely used dynamic  $\text{scCO}_2$  dyeing systems. The critical factors of dynamic  $\text{scCO}_2$  beam dyeing systems are porous beam and associated pipe connections in the high-pressure dyeing vessel. Porous beam is designed with a barrel with evenly distributed holes for uniformly forcing the dyeing fluid into the fabric under supercritical conditions. Meanwhile, the associated pipe connections can ensure the continuous circulation of the dyeing fluid during the  $\text{scCO}_2$  dyeing process.

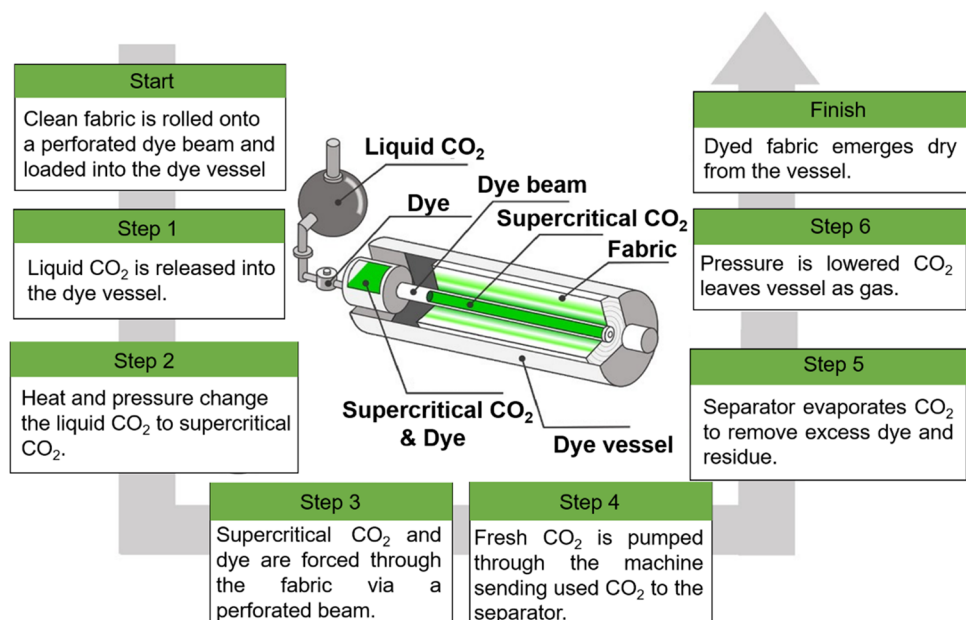
The basic structure and dyeing process is shown in Fig. 4 (Kim et al. 2018; Reji et al. 2019). Before dyeing, the fabric will be wrapped around the dye beam and then placed in the center of the dye vessel, which is connected with the inlet of the dyeing solution. The dyeing solution flows through the fabric by the holes on both sides of the dye beam and circulates by virtue of the circulating pump. Moreover, the flowing direction of the dyeing solution can be changed by the reversing device to ensure the dyeing uniformity of the inner and outer layers of the fabric. The dynamic  $\text{scCO}_2$  beam dyeing system has the characteristics of small dyeing vessel, simple structure, and convenient loading, which is beneficial for dyeing cloth and yarn. However, it also has certain limitations. With the increased amount of dyed fabric, the radius

of the dyed fabric wound on the dye beam will also increase, thus enhancing the resistance of the dyeing solution passing through the fabric. As a result, the dyeing speed will slow down and the uniformity will be influenced.

The dyeing efficiency of the traditional dynamic  $\text{scCO}_2$  beam dyeing systems is restricted by the gravity and the limited volume of the dyeing vessel. Designing horizontal beam dyeing vessel by employing the rotational drive shaft can efficiently avoid the gravity influence, and increasing the dyeing vessels to realize simultaneous multiple dyeing process leads to improved dyeing efficiency. Aiming at the issue, Gao et al. (2015) designed a high-efficiency  $\text{scCO}_2$  beam dyeing system with two beam dyeing vessels, which can dye two batches of fabrics independently and simultaneously. The horizontal beam dyeing vessel equips with the rotational drive shaft to ensure the continuous rotation of the wrap beam (Fig. S2a and b). This system can overcome the gravity influence during the dyeing process, thus achieving the high uniformity and production efficiency. The mobile driver section outside the vessel can actuate the movement of the cover, and the hydraulic lock device can fast lock the dyeing vessel cover to keep the air tightness of the whole dyeing process. Moreover, the double dyeing vessel system can overcome the defects that single-vessel system needs repetitive heating and gas venting to anew loading fabrics; as a result, the cost and  $\text{CO}_2$  gas consumption can be decreased.

It is worth noting that there are various types of textiles in the practical dyeing production, such as fabrics, skeins, garments, and balls. In the above systems, the fabrics are wrapped around the beam to achieve the dyeing process. However, the traditional beam cannot accommodate the loading need of skeins, garments, and balls; for that, they

**Fig. 4** Structure and working process of dyeing vessel in the dynamic supercritical carbon dioxide beam dyeing system (Kim et al. 2018). Before dyeing, the fabric will be wrapped around the dye beam and then placed in the center of the dye vessel, which is connected with the inlet of the dyeing solution. The dyeing solution flows through the fabric by the holes on both sides of the dye beam and circulates by virtue of the circulating pump



cannot be effectively wrapped around the beam. Considering the issue, the frame of the traditional beam dyeing vessel should be improved and specially designed for realizing different dyeing requirements. Zheng et al. (2015a) designed a special beam dyeing system to accomplish the uniform dyeing of loose fibers (Fig. S2c and d). The frame was designed as a tubular structure with inner porous cylinder, distributing porous tube and media channel to meet the need of the liquid flow, which made the best use of space in the dyeing vessel. It is worth noting that the system works with two dyeing modes. One is “inner dyeing/outer dyeing” mode that the fluid flows from the top of the dyeing vessel to penetrate fibers inside and then flows out at the bottom of the dyeing vessel, and another is “outer dyeing/ inner dyeing” mode that the dyeing solution enters from the bottom, adsorbed and dyed fibers from the outside of the dyeing frame. The alternant working modes can not only decrease the eddy of the dyeing solution but also increase the surface contact area of the dyeing solution and fibers, thus enhancing the dyeing rate and levelness.

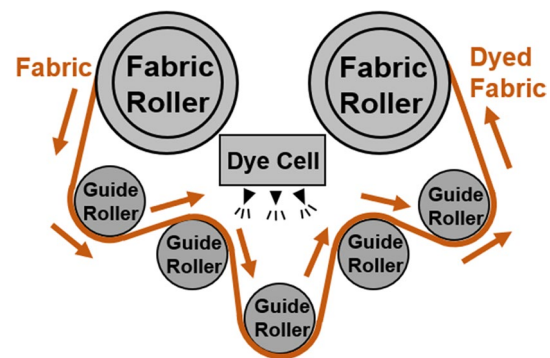
Moreover, in the traditional skein dyeing system, it is easy to produce friction between the yarns due to the lack of pores, thus influencing the dyeing uniformity. For this reason, Zheng et al. (2016) designed a scCO<sub>2</sub> skein dyeing system with double-ply parallel skein frame (Fig. S3a). During the process of scCO<sub>2</sub> skein dyeing, one part of the dyeing fluid flows through the beam to the skein frame and penetrates the skein from the middle to both sides, while another part enters the skein frame from the CO<sub>2</sub> overflow port, and then penetrates the skein from the bottom to top, thereby effectively improving the leveling performance of the skein. Besides, the dyeing demand of wool ball is large in the industrial dyeing systems but cannot be wrapped around the beam as ordinary fabrics, and the gravity factor has a great influence on the uniformity of wool ball dyeing. In order to change the gravity distribution and improve the dyeing uniformity of wool ball, a dynamic scCO<sub>2</sub> wool ball dyeing system was constructed (Fig. S3b) (Zheng et al. 2017a). There are four limit covers in the vessel, among which the first limit cover is used to control the amount of total wool balls and the other three limit covers are used to stratify the whole wool balls. The limit covers can be layered inside the dyeing vessel as needed in practical production. In addition, there are many micropores distributed on the limit cover, which can not only load the wool balls, but also ensure the circulation of dyeing liquid. The different dyeing vessel can be chosen according to actual dyeing needs of the fabric for efficient dyeing.

In the scCO<sub>2</sub> beam dyeing system, the dyeing uniformity of the fabric can be improved by reversing the flow direction of the dyeing liquid. However, reversing the flow direction of the dyeing liquid required the dyeing system having the reversing pipeline of high-pressure fluid, which increases

the risk of the dyeing process. As a result, scientists have developed the dynamic scCO<sub>2</sub> jig dyeing system, detailed in the next section.

### Dynamic jig dyeing system

In the scCO<sub>2</sub> beam dyeing system, the dyeing uniformity of the fabric can be improved by reversing the flow direction of the dyeing liquid. However, reversing the flow direction of the dyeing liquid required the dyeing system having the reversing pipeline of high-pressure fluid, which increases the risk of the dyeing process. Meanwhile, forcing the fabric to have reciprocating motion in the high-pressure dyeing vessel can effectively improve the dyeing uniformity and efficiency. Dynamic scCO<sub>2</sub> jig dyeing system was improved on the basis of the beam dyeing system, which added the fabric roller, guide roller, and the driver device in the dyeing vessel to realize the reciprocating motion of the fabric (Fig. 5). The fabric is wound around multiple guide rollers from one fabric roller and then connects to another fabric roller. While the supercritical fluid is dynamically circulated in the dyeing system, the fabric wound around the roller is also reciprocated in the dyeing vessel. After the dye dissolves in the supercritical fluid, the dyeing liquid will pass through and penetrate the fabric, which truly realizes the dynamic dyeing between the fabric and the dyeing solution. Generally speaking, the structure of the dynamic scCO<sub>2</sub> jig dyeing system is compact and reasonable, and the dynamic scCO<sub>2</sub> jig dyeing process combines the properties of supercritical fluid dyeing process and the characteristics of traditional water dyeing process, thus greatly improving the dyeing quality and efficiency. Nevertheless, the dynamic scCO<sub>2</sub> jig dyeing system has the disadvantages that the process of fabric wrapping and unloading is inconvenient and therefore needs to be further improved.



**Fig. 5** Dynamic supercritical carbon dioxide (scCO<sub>2</sub>) jig dyeing system. The fabric is wound around multiple guide rollers from one fabric roller and then connect to another fabric roller. While the supercritical fluid is dynamically circulated in the dyeing system, the fabric wound around the roller is also reciprocated in the dyeing vessel

Zhang et al. (2020) designed a horizontal scCO<sub>2</sub> jig dyeing system as shown in Fig. S4. This system equips with a supercritical fluid distributor between the guide rollers, from which the fabric can be penetrated evenly when it passes by. There are also two motors to drive the fabric rollers to unwind and rewind, respectively, as a constant speed during the dyeing process. After dyeing, the shell of the dyeing valve will slide along the guide rails, so that the fabric can be unloaded easily. Gao et al. (2022) further improved the system as shown in Fig. S5. The position of the guide rollers was changed and the dyeing liquid distributor was designed as the shape of conveyor belt, which make this system can be used in both ordinary jig dyeing and scCO<sub>2</sub> jig dyeing. For the ordinary dyeing, the fabric in the closed valve will not be polluted by the external debris, thus creating a cleaner dyeing environment. Furthermore, in the scCO<sub>2</sub> dyeing system, the unique valve space distribution and compact wrapping structure make the contact between the fabric and the dyeing liquid more sufficient, so that the dyeing uniformity and efficiency are improved.

For better contact between supercritical fluid and the fabric, Wang et al. (2014) improved the traditional scCO<sub>2</sub> jig dyeing system with spray nozzle in the dyeing vessel (Fig. S6). During the dyeing process, while the fabric is moving on the guide roller, scCO<sub>2</sub> dissolved with the dye will be sprayed out by the nozzle. After the rapid decompression and expansion, the dyeing liquid will pass through the fabric to accomplish the dyeing process, and then, scCO<sub>2</sub> with the remaining dyes will enter the recovery device and can be reused after the separation. Compared with the system where the dyeing liquid is controlled by the distributor, the spray nozzle can dye the fabric more precisely and in detail. Moreover, according to the specific dyeing requirements, the positions of the spray nozzle and the recycler can be adjusted, so as to realize single-side or double-side dyeing of the fabric. The scCO<sub>2</sub> spray dyeing system has the characteristics with simple structures, safe and convenient to operate, good dyeing levelness and continuity, and so on. However, the scCO<sub>2</sub> spray dyeing system generally relies on the high-pressure dyeing nozzle, so when scCO<sub>2</sub> is directly sprayed on the fabric without any protection measures, the fabric will be easily damaged by the high-pressure fluid jet. In order to overcome the disadvantages, Wang et al. (2012) designed a new type of scCO<sub>2</sub> spray dyeing system (Fig. S7). The system consists of squirrel-cage dyeing vessel and rolling dyeing rollers, which can realize dynamic contact dyeing between scCO<sub>2</sub> and the fabric. Moreover, the dyeing fabric is supported by the rolling dyeing rollers, which effectively eliminates the deformation and tension damage caused by the high-pressure fluid jet and traction force. Furthermore, for the light and deformable fabric dyeing, Yang et al. (2014) improved the scCO<sub>2</sub> spray dyeing system by combining the advantages of jig dyeing system and spray dyeing system

(Fig. S8). This scCO<sub>2</sub> spray dyeing system drives and circulates the fabric by the guide cable and eliminates the complex nozzle systems that avoids damage of the light fabrics. This scCO<sub>2</sub> spray dyeing system not only increases the contact area between the dyeing solution and the fabric, but also reduces the energy consumption of the circulation pump, especially suitable for high-volume dyeing production of deformable fabrics.

In a summary, the scCO<sub>2</sub> dyeing systems are generally divided into static dyeing system, dynamic beam dyeing system, and dynamic jig dyeing system, according to whether the dyeing liquid and the fabric are dynamically circulated during the dyeing process. Static dyeing system is mainly consisted of CO<sub>2</sub> cylinder and pump, temperature and pressure controller, and the dyeing vessel. Static dyeing system is easy to operate and suitable for using in the laboratory-scale dyeing experiments to study the effect of parameters on the dyeing of different fabrics during the scCO<sub>2</sub> dyeing process. Dynamic dyeing system additionally adds a circulation system and a recycling device on the basis of the static dyeing system. Moreover, the dynamic beam dyeing system and the dynamic jig dyeing system show difference on the dyeing vessel, which matched with the specific dyeing requirements. Dynamic dyeing system has higher dyeing efficiency and is more suitable for large-scale practical industrial production. Different types of fabric dyed in different scCO<sub>2</sub> dyeing systems and the corresponding dyeing conditions are summarized in Table 1.

Moreover, it is worth noting that scCO<sub>2</sub> dyeing process may affect the properties of the dyeing fabric, which generates the resulting need for the design and operation of the scCO<sub>2</sub> dyeing system. The scCO<sub>2</sub> dyeing process contains the rapid pressurization and depressurization step, and the depressurization rate turns into an important factor affecting the properties of the dyeing fabric. Zheng et al. (2017b) investigated the influence of the depressurization rate on the properties of yak hairs and found that the breaking strength and the elongation at break of the yak hairs both increased with the increasing depressurization rate. The result may attribute to the rapid air flow during the pressurization step and depressurization step during the scCO<sub>2</sub> dyeing process. The pressurization process is realized by operating the fixed-frequency high-pressure pump, while the depressurization process is achieved by the valve control leading to relatively irregular pressure decreasing rate. Consequently, the torsion, bending, and shearing action for the yak hair strengthens when the depressurization rate increases, especially in the depressurization step during the scCO<sub>2</sub> dyeing process.

Meanwhile, the surface fiber morphology may also be affected during the high-pressure process, of which the surface of the dyeing fabric may be altered to be rougher with the appearance of stripes and wrinkles. Zheng et al. (2015b) observed the same conclusion when studying the influence



**Table 1** Fabric dyed in different scCO<sub>2</sub> dyeing systems and the associated dyeing conditions

Fabric	Type of dyeing system	Temperature (°C)	Pressure (Mpa)	Time (min)	References
Cotton	Static	30–120	12–30	30–120	Zhang et al. (2017)
Cotton	Dynamic	60–120	20	60–180	Yang et al. (2017)
Cotton, wool, silk	Static	110	26	Not reported	Liu et al. (2018)
Cotton, wool, silk	Dynamic	130	20	Not reported	Yan et al. (2020)
Wool	Static	120	20	90	Zhang et al. (2016)
Wool	Dynamic	70–120	15–35	30–180	Zheng et al. (2017a)
Yak hair	Dynamic	80–120	21–25	40–80	Zheng et al. (2017b)
Polyester, cotton	Dynamic	80	18	60	Gao et al. (2015)
Polyester	Dynamic	60–140	15–35	20–100	Xiong et al. (2017)
Polyester	Static	120	25	60	Abate et al. (2020)
Polyester	Static/Dynamic	100–120	24	60	Zheng et al. (2016)
Nylon 6, Polyester	Dynamic	100–130	15–25	60–120	Abou et al. (2018b)
Nylon 6, Polyester	Static	100–130	15–25	60–180	Abou et al. (2019a)
Nylon 6	Dynamic	80–120	5–15	60–180	Abou et al. (2015)
Polypropylene	Dynamic	100–130	15–25	60–180	Abou et al. (2018c)
Polypropylene	Static	110–130	15–25	60–120	Abou et al. (2019b)
Zipper tape	Dynamic	90	23	60	Huang et al. (2017)
Zipper tape	Dynamic	70–110	14–25	20–65	Huang et al. (2019)
Ultra-high-molecular-weight polyethylene fiber	Static	120	28.85	60	Zhou et al. (2023)
Wood	Static	45–100	10–30	900	Jaxel et al. (2020)
Ramie fiber	Static	70–130	12–20	90	Liu et al. (2006)

of depressurization rate on the morphology of the wool fiber, and the results investigated that the fiber damage and brightness variation would be higher with the increased depressurization rate. The phenomenon can be attributed to the burst of water droplets by the fast pressure release, which can be effectively overcome by precisely controlling and slowing down the depressurization rate. As a consequent, for avoiding the deterioration of mechanical and physical properties of the dyeing fabric, the scCO<sub>2</sub> dyeing system should be equipped with depressurization rate controlling device to precisely release the pressure with a fixed frequency in control. Moreover, the depressurization rate should be set at different values when dyeing different fabrics for obtaining optimized properties.

In addition, particles formation on the dyeing fabric during the scCO<sub>2</sub> dyeing process has also been observed in several research. Gao et al. (2015) found the particles presented on the surface of the dyeing fabric after the scCO<sub>2</sub> dyeing process attributed to the deposition of active compounds in the dye solution. Abate et al. (2019) reported the particles formed on dyeing fibers due to the oligomer crystals produced by the migration of these molecules to the surface, which was caused by CO<sub>2</sub> penetration and high-temperature process. The same phenomenon was also observed in nicotinamide dyeing for viscose fabric and azo-based dispersed dyes for dyeing wool and cotton fabrics. However, it is worth

noting that no obvious presence of the formed particles was detected when using the gallic acid with higher diffusion rate due to its smaller size than other dyes in the same conditions. Enhancing the fiber swelling by suitable operation of the scCO<sub>2</sub> dyeing system can lead to a better penetration of the dye into fabric instead of deposition at the surface of the fabric. Consequently, for avoiding the particle deposition of the high molecular weight compounds on the dyeing fabric during the scCO<sub>2</sub> dyeing process, the scCO<sub>2</sub> dyeing system should be designed with depressurization controlling device to precisely release the pressure in the dyeing vessel for avoiding the nucleation, or operating suitable supercritical fluid flow patterns in the dyeing vessel to enhance the diffusion rate of the dyes into the fabric. Moreover, it is also important to design the scCO<sub>2</sub> dyeing system with recirculation filter for filtration of the recirculation current to effectively eliminate the suspended particles, as well as improve the CO<sub>2</sub>/dye separators for better separation efficiency of CO<sub>2</sub> and the dye.

Overall, scCO<sub>2</sub> dyeing technology has been identified as an attractive alternative to water-based dyeing. The low mass transfer resistance and high diffusion rates observed in scCO<sub>2</sub> assist dye penetration into the fibers causing a reduction on dyeing times. Besides, CO<sub>2</sub> completely vaporizes by depressurization, and therefore, no subsequent drying or solvent removal operations are required. The rational design

of scCO<sub>2</sub> dyeing system is the key of scCO<sub>2</sub> dyeing technology applied in practical production. However, current scCO<sub>2</sub> dyeing systems have the problems that different types of fabric and dyes, the geometric design of the dyeing vessel, and the flow conditions of scCO<sub>2</sub> will all influence the dyeing uniformity during the scCO<sub>2</sub> dyeing process. Therefore, carrying out the computational simulation of fluid dynamics of scCO<sub>2</sub> flow in different types of scCO<sub>2</sub> dyeing systems is necessary for analyzing the effect of operation conditions on the dyeing uniformity during the scCO<sub>2</sub> dyeing process, as well as for contrapuntally designing the dyeing conditions of different types of fabrics. Moreover, the residual dye particles in the pipelines of the systems during the scCO<sub>2</sub> dyeing process will pollute the fabric after the dye changes in the subsequent dyeing process. Designing novel separator that can provide lower pressure drop corresponding to higher separation efficiency is crucial for solving the CO<sub>2</sub> recontamination and color reproducibility problems. In addition, visualization of the scCO<sub>2</sub> dyeing process is crucial for judging the color presentation degree and dyeing quality, which requires visual scCO<sub>2</sub> dyeing systems should be more focused and developed for the future improvement of the scCO<sub>2</sub> dyeing systems.

## Extraction systems

With the increasing demand of natural products, more selective and effective extraction technology is required to extract the ingredients from raw materials (Reverchon and Senatore 1992). The supercritical fluid extraction (SFE) technology has been developed as a substitute for traditional solvent-based techniques (Sahena et al. 2009). SFE is referred to a process in which the extracted component is separated or dissolved from the raw materials by the supercritical fluid according to their dissolution properties (Spanos et al. 1993). The solubility of the extracted components can be maintained by varying the temperature and pressure above the critical point (Zougagh et al. 2004). The SFE technology has the advantages of selective extraction, high extraction efficiencies, easy separation, short processing time, and low impact on the environment, which paves the way to selectively and mildly extract the ingredients from the natural materials (Attard et al. 2016). When scCO<sub>2</sub> is used, many components can be extracted in a short time, and there is no residual solvent after the extraction process (Herrero et al. 2010). During the scCO<sub>2</sub> extraction process, the liquid-like density provides a good solvating power, while the gas-like high diffusivity and low viscosity lead to the deep penetration into the matrix. As a result, the rate of mass transfer into scCO<sub>2</sub> is higher than that into the liquid (Chassagnez-Mendez et al. 2000; Silva et al. 2017; Vladić et al. 2021). In addition, scCO<sub>2</sub> can be applied in the extraction of both

polar compounds and non-polar compounds. ScCO<sub>2</sub> as non-polar compound is a good solvent for non-polar compounds extraction, such as essential oils, hydrocarbons, and organic pesticides (Chassagnez-Mendez et al. 2000; Fornari et al. 2012; Mouahid et al. 2013; Tyśkiewicz et al. 2018). Moreover, the addition of polar cosolvents, such as ethanol and methanol, can effectively increase the solubility of polar compounds in scCO<sub>2</sub>, thus overcoming the disadvantages of low affinity with polar compounds (Devi and Khanam 2019; Fujii et al. 2018; Soh et al. 2019). With more and more extensive application of scCO<sub>2</sub> extraction, the corresponding systems are also improved continuously.

ScCO<sub>2</sub> extraction process typically requires continuous production proceeded under high-pressure conditions, and therefore, the rational design of scCO<sub>2</sub> extraction system has become the research focus in recent years. ScCO<sub>2</sub> dyeing systems should satisfy the requirements that the components to be extracted can be effectively dissolved into scCO<sub>2</sub> under desired constant temperature and pressure conditions, and scCO<sub>2</sub> should be evenly distributed and fully contacted with the extract at any cross section of the extraction vessel to ensure the extract purity, which can be realized by equipping backpressure regulator (BPR) and high-pressure sealed screw feed device, respectively. ScCO<sub>2</sub> dyeing systems can be divided into batch extraction system and semicontinuous extraction system. Moreover, multiple-separator extraction systems were designed to realize multiple extraction of the same or different components for obtaining improved extraction efficiency. Different types of scCO<sub>2</sub> dyeing systems will be introduced separately in the following.

### Batch extraction system

ScCO<sub>2</sub> batch extraction systems are the traditional extraction systems that most widely used in laboratory-scale extraction of various types of components. ScCO<sub>2</sub> batch extraction systems should be designed with high-pressure vessel, temperature- and pressure-controlling device, and the separator to collect the extracted components. Moreover, when adding the raw materials into the extraction vessel and taking out of the extracted components from the extraction vessel, the extraction vessel needs to be opened and closed frequently. In order to realize facilitate operation and shorten operation time, the extraction vessel should equip with quick-opening device. ScCO<sub>2</sub> dynamic extraction systems are simply designed and easy to operate and can maintain the constant extraction conditions in the extraction vessel, which is beneficial to measure the extraction rate and extraction influence of parameters, such as extraction temperature, pressure, scCO<sub>2</sub> flow rate, concentration, and particle size of raw materials.

Naikoo et al. (2021) used the typical batch scCO<sub>2</sub> extraction system to extract fat-soluble vitamin A from retinol

(Fig. 6). The system is composed with CO<sub>2</sub> tank, refrigerator, high-pressure pump, heating device, extractor, and cosolvent tank that can be set according to actual needs. The scCO<sub>2</sub> extraction process is as follows. Liquid CO<sub>2</sub> is firstly cooled at low temperature by the refrigerator and mixed with the cosolvent of methanol, and then, CO<sub>2</sub> and the cosolvent are further mixed through the spiral tube. Before entering the extractor, CO<sub>2</sub> will be preheated to the desired extraction temperature and then enters the extractor to react with retinol for the extraction of fat-soluble vitamin A. This typical scCO<sub>2</sub> extraction system has been widely used due to its properties of simple, extensively applicable and easy to control. Mouahid et al. (2013) used this scCO<sub>2</sub> extraction system to study the extraction modeling curves of four different microalgae, which aims to verify that Sovová equation could be applied to all microalgal extraction cases. Khaw et al. (2019) used the system for scCO<sub>2</sub> extraction of freeze-dried leaf juice from *Carica papaya* and further investigated the maximal extract activity at the best small-scale extraction parameters. Györi et al. (2019) extracted the aroma compounds from herbs and spices by this static scCO<sub>2</sub> extraction system. It was found that the extraction efficiency, the number of extracted compounds, and the quality of product from scCO<sub>2</sub> extraction are all higher than those from classic maceration. Chassagnez-Mendez et al. (2000) studied the influence of temperature and cosolvent on turmeric extraction by this typical scCO<sub>2</sub> extraction system. Moreover, different types of components extracted in batch extraction system and the corresponding extraction conditions are summarized in Table 2.

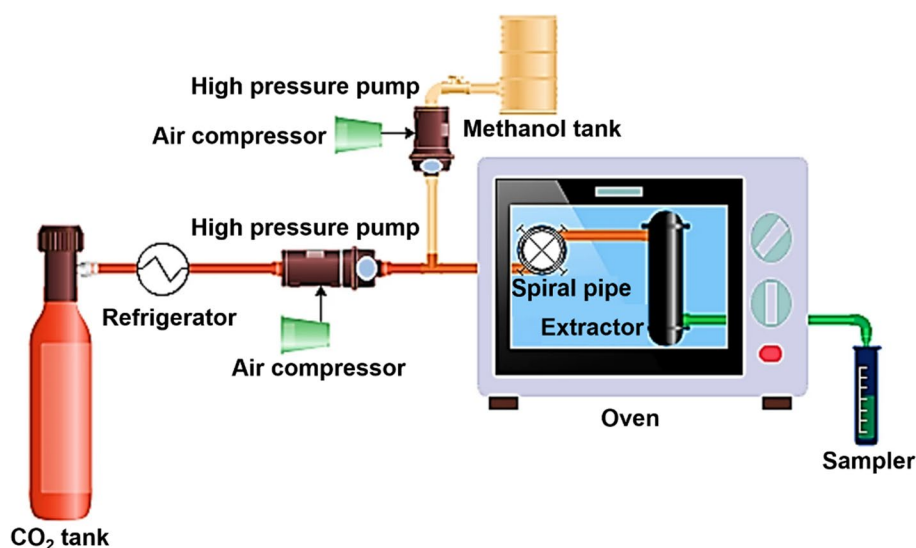
### Semicontinuous extraction system

In the traditional batch extraction systems, high CO<sub>2</sub> flow rate can increase mass transfer driving force, thus

improving the extraction rate and reducing the extraction time. However, high CO<sub>2</sub> flow rate also leads to inadequate contact between the extract components and scCO<sub>2</sub>, which greatly affects the extraction efficiency. Meanwhile, the extraction vessel needs to be opened and closed frequently to load the raw materials during the static extraction process, thus leading to complex extraction operation and long extraction time. Aiming at the issue, semicontinuous extraction systems are improved on the basis of batch extraction system by adding BPR and CO<sub>2</sub> recycling device to realize static and dynamic alternating extraction. The critical factors of semicontinuous extraction systems are rational design of the extraction vessel for simultaneously realizing maintaining constant high pressure in the extraction vessel and also ensuring the continuous flow of the raw materials and extracted components into and out of the extraction vessel, which can be realized by utilizing high-pressure sealed screw feed device for extracting components from solid extracts and by employing high-pressure injector to extract liquid components.

The traditional batch extraction system has been improved by adding BPR and a CO<sub>2</sub> recycling device to allow smooth alternating of static extraction and dynamic extraction, and to realize CO<sub>2</sub> recycle (Fig. S9) (Ghoreishi et al. 2009). During the scCO<sub>2</sub> extraction process, after CO<sub>2</sub> is injected into the extraction column, the BPR will be set to the appropriate working pressure. Simultaneously, the temperature will be maintained through the coil preheater and oven. When the required pressure and temperature are reached in the extraction column, the pump and the valve will be disconnected. Subsequently, scCO<sub>2</sub> can dissolve the ingredients during the static extraction time, and then flow at the set rate after extraction. The dissolved ingredients are trapped in the collection vessel and CO<sub>2</sub> is recycled by the circulation device. The alternating static extraction and dynamic extraction

**Fig. 6** Batch supercritical carbon dioxide (scCO<sub>2</sub>) extraction system designed by Naikoo et al (2021). Liquid CO<sub>2</sub> is firstly cooled at low temperature by the refrigerator and mixed with the cosolvent, and then, CO<sub>2</sub> and the cosolvent are further mixed through the spiral pipe. Before entering the extractor, CO<sub>2</sub> will be preheated to the desired extraction temperature and then enters the extractor to react with retinol for the extraction of fat-soluble vitamin A



**Table 2** Components extracted in batch extraction system and the associated extraction conditions

Target compound	Source	Temperature (°C)	Pressure (Mpa)	CO <sub>2</sub> flow rate (L min <sup>-1</sup> )	References
Lycopene and β-carotene	Tomato skins	80	30	6.7	Sabio et al. (2003)
Fat-soluble vitamin A	Retinol	30–50	9–23.5	Not reported	Naikoo et al. (2021)
Carotenoids	Carrots	70	55.1	2	Sun and Temelli (2006)
Neutral lipids	Microalgae	60	40	2.5–4.2	Mouahid et al. (2013)
Lycopene	Dried pomace of tomato	40–80	30–46	Not reported	Vági et al. (2007)
Total carotenoids	Dried pomace of tomato	40–80	38–46	Not reported	Vági et al. (2007)
Selective cytotoxic activity on squamous cell carcinoma	Freeze-dried leaf juice of Carica papaya	35–50	8.5–25	Not reported	Khaw et al. (2019)
Lycopene	Tomato skin	40–100	20–50	0.0025	Topal et al. (2006)
Aroma compounds	Herbs and spices	50	18	Not reported	Györi et al. (2019)
Polyphenols	Grape waste	50.5	25	0.85	Lazze et al. (2009)
Curcumins and essential oil	Rhizomes of turmeric	40 and 45	25 and 30	Not reported	Chassagnez et al. (2000)
Limonin, limonin-17-β-D-glucopyranoside, and flavonoid naringin	Grapefruit seeds	50	48.3	5	Yu et al. (2007)
		50	41.4	5	
		60	41.4	5	
Tocopherol	Pomegranate	50	30	Not reported	Liu et al. (2009)
Anthocyanins, proanthocyanidins, flavonols, catechins, and benzoic and cinnamic acids	Raspberry pomace, cranberry pomace, blueberry pomace	60	20 and 25	0.042	Laroze et al. (2010)
Furocoumarins	Celeriacs	35–80	12–25	0.0026–0.0028	Järvenpää et al. (1997)
Pigment components, such as lutein, β-carotene, chlorophyll a, and chlorophyll b	Chlorella vulgaris	60–80	20–50	0.0025	Kitadaä et al. (2009)
Fatty oil	Flaxseed	50	30	Not reported	Pradhan et al. (2010)
Sunflower oil	Sunflower seeds	40–80	20–60	0.001–0.006	Salgin et al. (2006)

process can increase the scCO<sub>2</sub>-assisted extraction time, thus improving the extraction rate and efficiency.

Soh et al. (2019) used the semicontinuous extraction system to study how the pressure, temperature, and flow rate influence the scCO<sub>2</sub> extraction of patchouli oil. It was found that higher pressure and flow rate would increase the extraction rate, while higher temperature had an inverse effect for the extraction process. Fujii et al. (2018) developed an analogous system, in which the cosolvent was replaced with liquid solution to form the liquid–CO<sub>2</sub> emulsion in the micro-mixing device, thus increasing the mass transfer from liquid to scCO<sub>2</sub>. This system could fast and continuously extract vanillin from aqueous vanillin solution and also could be applied in other aqueous liquids containing hydrophobic compounds. Moreover, Cornelio-Santiago et al. (2017) measured the scCO<sub>2</sub> extraction solubility of oil from green coffee by the semicontinuous extraction system. Fornari et al. (2012) extracted the essential oil from different herbs and plants using the semicontinuous extraction system. Devi and Khanam (2019) utilized the semicontinuous extraction system for the extraction of ω-3 α-linolenic and

ω-6 linoleic acids from hemp seed in scCO<sub>2</sub> and further optimized the process parameters. Andersen and Bruno (2003) used this semicontinuous extraction system to extract metal β-diketonate complexes from aqueous solutions, which overcame the limited mass transfer between the CO<sub>2</sub>-soluble chelating agent and the water-soluble metal ion.

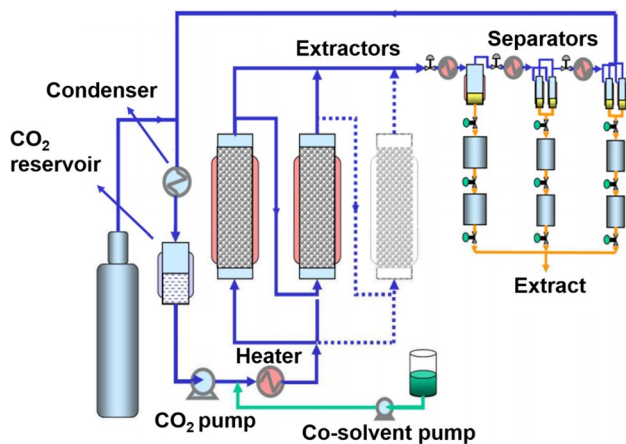
### Multiple-separator extraction system

The volume of the extraction vessel also limits the extraction efficiency in the practical production process. ScCO<sub>2</sub> extraction systems are mainly small or medium sized; for that, big volume of the extraction vessel requires high CO<sub>2</sub> consumption and long pressurization time and also increases the operation difficulties. Aiming at the issue, multiple extraction vessels and separators can be employed to further improve the extraction efficiency. Multiple extraction vessels can be connected in series to extract the same components repeatedly for enhancing the extraction purity and also can be connected in parallel to extract the same components for improving the extraction rate or extract different

components in different extraction vessels simultaneously. Moreover, multiple separators are equipped connected with the multiple extraction vessels to separate the same or different components correspondingly and also can evaluate the separation extent and extraction efficiency.

Rochfort et al. (2020) and Srinivas et al. (2017) further improved the above system to achieve multicomponent separation and evaluate the separation extent (Figs. 7 and S10). The improved system is equipped with an automatic backpressure regulator (ABPR) for automatically regulating the temperature and pressure in the extraction vessel and also added three independent-heated cyclone separators for further separation of the ingredients. Moreover, the temperature and pressure in three cyclone separators are independently and accurately controlled by three manually adjusted BPR, which not only could measure the separation extent of different categories in each cyclonic separator, but also could evaluate the extraction efficiency of the same category by combining the ingredients together.

In addition to the continuous improvement of the extraction process, the design of the extraction reactor is also critical. The original design of the Nottingham reactor is based on a syringe compressor that can convert liquid CO<sub>2</sub> to scCO<sub>2</sub> (Fig. 8a) (Qamar et al. 2021). ScCO<sub>2</sub> enters from the top of the extraction chamber where glass wool and stainless steel filter are used to separate the ingredients from the raw materials. However, the disadvantage of this extraction reactor is that a large amount of ingredients will remain on the glass wool which reduces the extraction yield seriously, and there is also a problem of raw material pollution



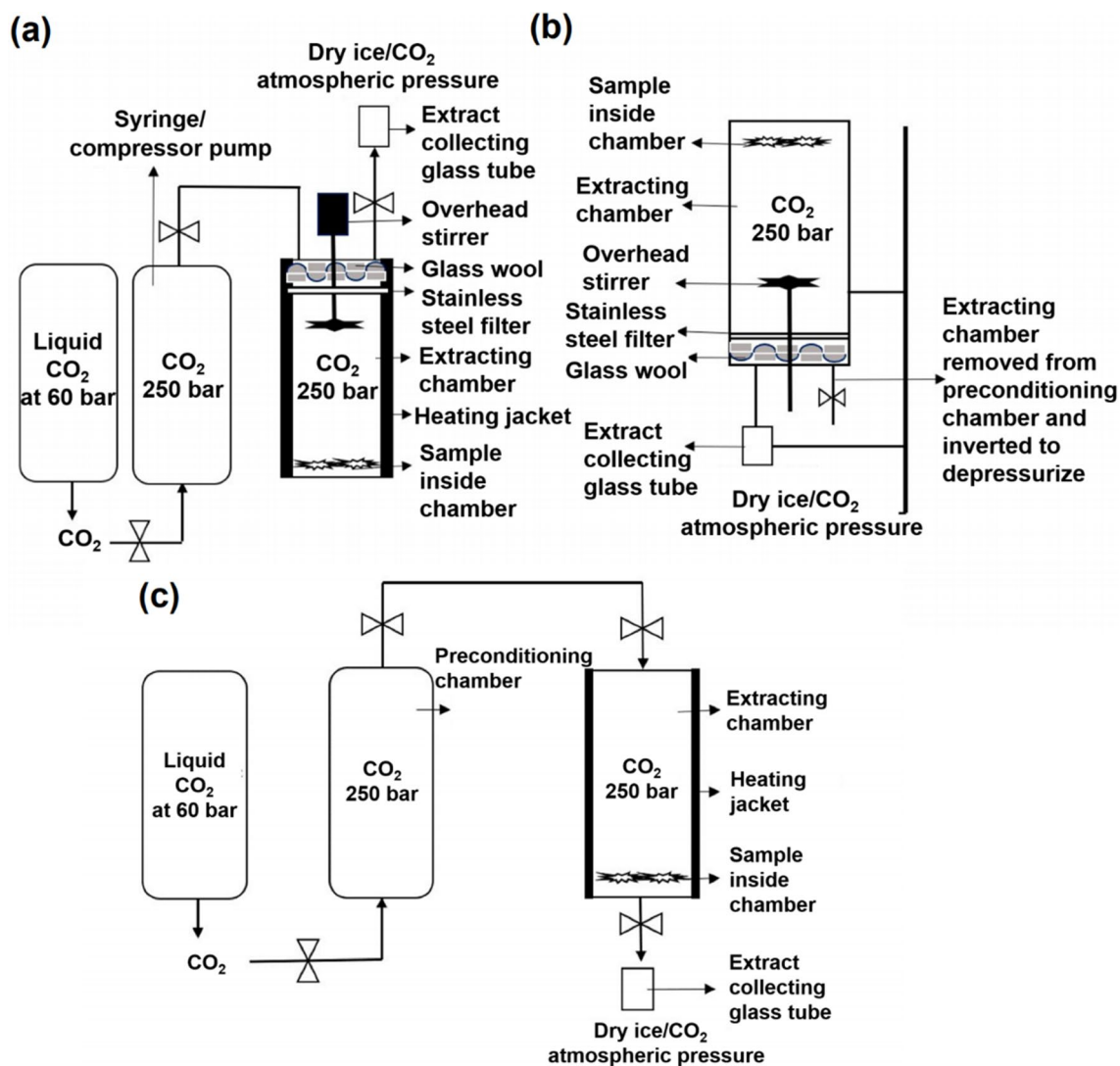
**Fig. 7** Supercritical carbon dioxide (scCO<sub>2</sub>) extraction system with independent separators (Srinivas et al. 2017). The temperature and pressure in three cyclone separators are independently and accurately controlled by three manually adjusted backpressure regulator (BPR), which not only could measure the separation extent of different categories in each cyclonic separator, but also could evaluate the extraction efficiency of the same category by combining the ingredients together

to be resolved. In order to solve the above problems, after the extraction is completed, the extraction chamber will be removed from preconditioning chamber and inverted to depressurize with the help of bracket (Fig. 8b). Because the extraction chamber is completely depressurized at 0 bar, the ingredients can be separated with a larger extent, thus improving the extraction efficiency. However, the problem of serious raw material pollution has not been completely resolved. Therefore, the helix reactor with low-pressure regulation chamber was designed (Fig. 8c) (Qamar et al. 2021), where the backpressure is directly regulated by the liquid CO<sub>2</sub> cylinder and the preconditioning chamber. During the scCO<sub>2</sub> extraction process, CO<sub>2</sub> enters and extracts from the bottom of the extracting chamber and then the extracted components are separated from the raw materials by the built-in standard filter at the top of the extracting chamber. After the extraction is completed, CO<sub>2</sub> dissolved the matrix will enter the separating chamber, where the pressure is about 50 bar to avoid the piston effect of dry ice. Finally, the ingredients will be collected in the extract collecting glass tube. The helix reactor can not only improve the extraction efficiency, but also avoid the raw material contamination problems, which is suitable for extraction requirements with high quality and high extraction rate.

To sum up, the scCO<sub>2</sub>-assisted extraction systems are split into typical static extraction system, static and dynamic alternating extraction system, and multiple-separator extraction system. The typical static extraction system is consisted of CO<sub>2</sub> supply and pump device, temperature- and pressure-controlling device, and the extraction vessel. Static and dynamic alternating extraction system is improved on the typical static extraction system by adding BPR and CO<sub>2</sub> recycling device. Static and dynamic alternating extraction system has high extraction efficiency and is widely used for most of the extraction requirements. The multiple-separator extraction system is added with several independent-heated cyclone separators on the basis of the typical static extraction system and can realize multicomponent separation and evaluate the separation extent.

Overall, scCO<sub>2</sub> extraction technology has obtained increasing attention in the fields of fractionation of liquid mixtures and solid material extraction due to its fascinating properties of high density, low viscosity, zero surface tension, and adjustable properties by manipulating the pressure and temperature. Now, more and more attention has been paid on the development of scCO<sub>2</sub> extraction processes and corresponding systems and also attracted interests of industries on scCO<sub>2</sub> extraction techniques. However, current scCO<sub>2</sub> extraction systems also face several challenges to be further solved and thus more suitable to apply in the practical industry production. In scCO<sub>2</sub> extraction process, the particle size of raw materials will affect the extraction efficiency, of which the contact area between the extracted





**Fig. 8** **a** Supercritical fluid extraction Nottingham reactor. Supercritical carbon dioxide (scCO<sub>2</sub>) enters from the top of the extraction chamber where glass wool and stainless steel filter are used to separate the ingredients from the raw materials. **b** Sample-containing chamber inverted and placed on stirrer for the depressurization. After the extraction is completed, the extraction chamber will be removed

from preconditioning chamber and inverted to depressurize with the help of bracket and **c** schematic representation of the Helix reactor (Qamar et al. 2021). After the extraction is completed, CO<sub>2</sub> dissolved the matrix will enter the separating chamber, and the ingredients will be collected in the extract collecting glass tube

component and scCO<sub>2</sub> will increase when the particle size of raw materials decreases, thus leading to enhanced extraction efficiency. However, small particle size of raw materials will not only result in serious blockage of the sieve pore, but also cause the plug of the filter at the exit of the extraction vessel. Meanwhile, when the extracted components are powder materials, the pressed powder under high pressure and temperature will seriously wear the seals of the high-pressure extraction vessel, which requires the seals of the high-pressure extraction vessel possessing strong wear resistance to maintain the stable pressure during the whole scCO<sub>2</sub> extraction process. Moreover, in scCO<sub>2</sub> extraction process, the water cannot be thoroughly removed, thus

accumulating more and more water with the cycle, which may influence the extract purity and efficiency. The existing scCO<sub>2</sub> extraction system usually equips with drain hole or relies on adding desiccant, which has the disadvantages of poor water removal effect and inconvenient replacement of the desiccant. Improving the scCO<sub>2</sub> extraction system with unique water removal device will effectively enhance the extract purity and efficiency. It is also worth noting that dynamic scCO<sub>2</sub> extraction system can improve the extraction efficiency due to the circulation of scCO<sub>2</sub> compared with static scCO<sub>2</sub> extraction system. However, the dynamic scCO<sub>2</sub> extraction system has the problems that the pressure fluctuation in the high-pressure extraction vessel will be

caused by CO<sub>2</sub> circulation process. Therefore, improving the dynamic scCO<sub>2</sub> extraction system with pressure precisely controlling device to maintain the constant pressure during the whole extraction process is necessary.

## Chromatographic systems

The availability of efficient analytical separation tools is critical to the pharmaceutical industry; as a result, various chromatographic techniques, such as high performance liquid chromatograph (HPLC), gas chromatograph (GC), and supercritical fluid chromatograph (SFC), are commonly used for the purpose. Among them, SFC has attracted attention in recent years (Tavares and Lanças 2000; Van et al. 2018; Zheng et al. 2020). When the temperature and pressure of the mobile phase in SFC are higher than the critical point, the solvating power of the mobile phase will be changed to achieve the separation of certain components (Desfontaine et al. 2015; Gao et al. 2017; He et al. 2018). The parameters of temperature, pressure, and modifier content during SFC process, compared with GC and HPLC processes, can be controlled independently or cooperatively (Heiland et al. 2019; Lu et al. 2006; Planeta and Roth 2004; Zheng et al. 2020). Moreover, the supercritical fluid with gas-like viscosity and diffusivity can still maintain high separation efficiency at high mobile phase velocities, and its liquid-like density and solvating power can also provide fast transfer and good solubility of analytes, which is beneficial for chromatography and purification in food or pharmaceutical analysis (Ehlers et al. 1998; Hawthorne and Miller 1986; Taylor 2009). Among the supercritical fluid, scCO<sub>2</sub> with the characteristics of low solvent toxicity, low critical temperature, chemical inertness, and nonflammability has become the preferred mobile phase in SFC technique. Furthermore, the addition of modifiers can overcome the limited solubility of polar compounds in non-polar scCO<sub>2</sub>, thus greatly expanding the application in pharmaceutical field (Gere 1983).

SFC utilizes scCO<sub>2</sub> as the mobile phase during the chromatography process and employed porous solid particles in the chromatography column. When the mobile phase carrying the samples continuously impacts the stationary phase, the components to be separated in the samples will be simultaneously subjected to the thrust and gravity of the mobile phase. Due to the combined action of these two forces, the mobile phase carrying the samples will go through “adsorption-elution-adsorption-re-elution” process repeatedly. If a substance in the sample is closely bound to the stationary phase, the repressor force will be high, and the migration rate will be slow. Otherwise, the migration rate will be fast. Then, the speed of each substance movement will be different due to the difference of repressor force,

thus leading to different staying time of each substance in the chromatography column, so as to realize the separation of each component in the samples. SFC systems are gradually developed to become commercialized. In the 1980s, the SFC systems were mainly divided into two types, i.e., open tubular capillary column (GC-like chromatograph) system and packed column (LC-like chromatograph) system, which were exclusively home-made by retrofitting GC or LC system for around 20 years (Pyo 2001). In 1992, HP supplier invented a new SFC system with a dynamic compressibility compensation and electronic BPR. Since then, more suppliers offered different SFC systems, such as Shimadzu, Jasco, and Fluitron, which has been commercialized successfully.

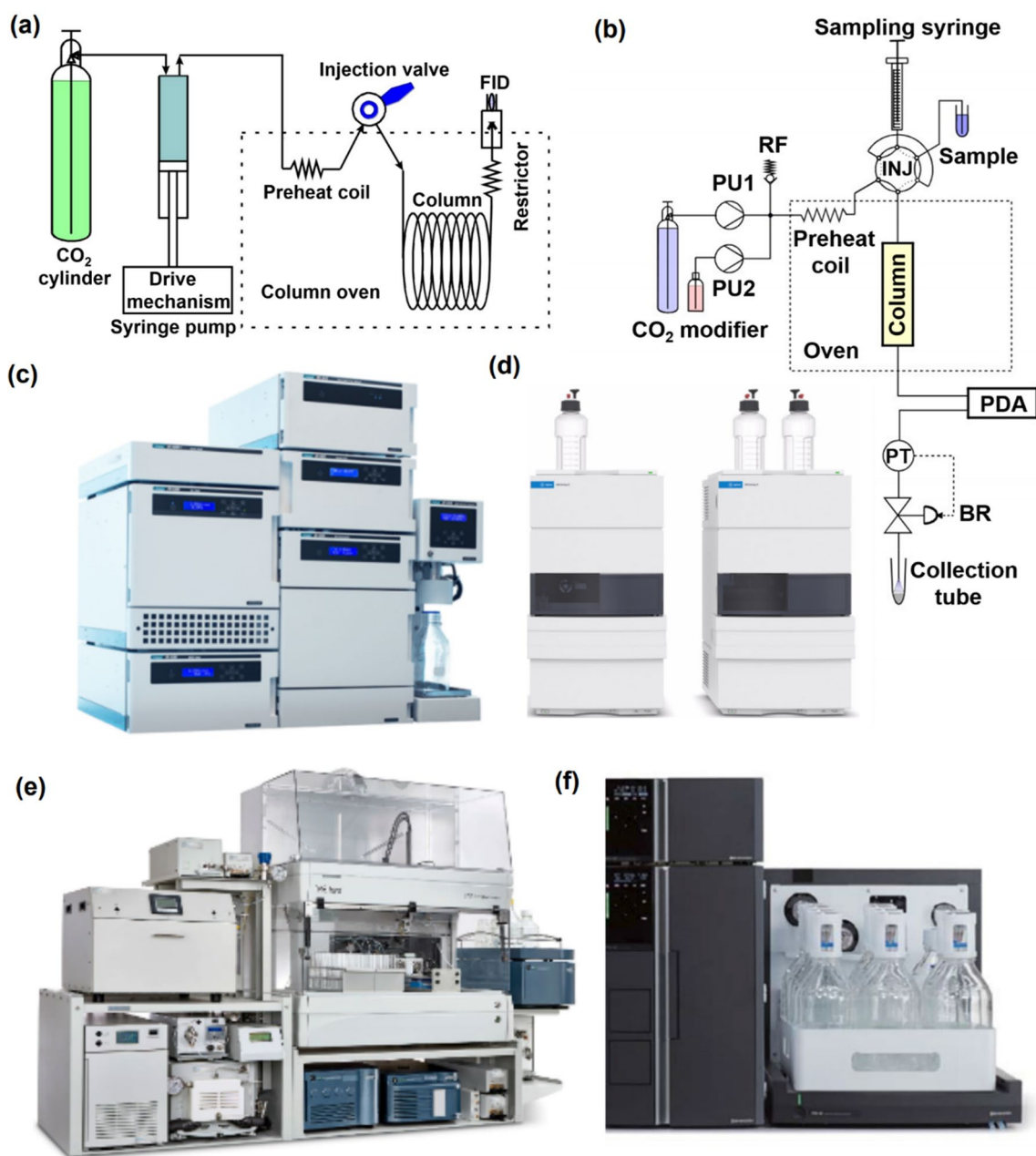
### Open tubular capillary column system

Novotny et al. designed the open tubular capillary column SFC in 1981, which was a fused-silica capillary tube with 50 μm inner diameter and coated with polymer as the stationary phase. The open tubular capillary column SFC system is equipped with syringe pump for delivering and pressurizing CO<sub>2</sub>, injection valve for introducing samples, GC-like oven, wall-coated open tubular column, fixed restrictor for maintaining the mobile phase at supercritical state and flame ionization detector (FID) (Fig. 9a) (Saito 2013), and the open tubular capillary column SFC system has been exclusively marketed and patented by Lee Scientific.

The open tubular capillary column SFC system is equipped with syringe pump, injection valve, GC-like oven, wall-coated open tubular column, fixed restrictor, and flame ionization detector (FID) (Fig. 9a) (Saito 2013), and the open tubular capillary column SFC system has been exclusively marketed and patented by Lee Scientific. In this system, the backpressure is controlled by the restrictor with a certain flow rate, which can ensure the system pressure above the critical pressure of CO<sub>2</sub> to keep supercritical state. However, under the circumstances, pressure as the most important parameter will be restricted by the flow rate, which cannot be changed independently. Therefore, the optimum flow rate cannot be obtained at the optimum pressure. In addition, when the organic modifiers are used to increase the polarity of scCO<sub>2</sub>, excessive baseline background will be produced and thus limit the application of standard FID detectors (Pyo and Lee 1999). Thus, the open tubular capillary column SFC systems declined rapidly in the early 1990s.

### Packed column system

It is worth noting that almost all SFC research works were proceeded by utilizing packed column SFC before the open tubular capillary column SFC was introduced. Packed column SFC was LC-like instrument while open tubular capillary column SFC was more like GC. Although open tubular



**Fig. 9** **a** Typical gas chromatograph (GC)-like open tubular column supercritical fluid chromatograph (SFC) system. FID. Flame ionization detector. Reproduced with permission of Elsevier from Saito (2013); **b** typical liquid chromatograph (LC)-like packed column SFC system. PU1. Liquefied CO<sub>2</sub> delivery reciprocating pump with chilled pump heads, PU2. Modifier solvent delivery pump, RF. Safety relief valve that prevents over pressure, INJ. Injection valve, PDA.

Photodiode array, PT. Pressure transducer, BR. Backpressure regulator. Reproduced with permission of Elsevier from ref. (Saito 2013); **c** SFC-4000 analytical chromatograph designed by Jasco; **d** 1260 Infinity II analytical SFC system designed by Agilent Technologies; **e** Prep 150 AP preparative SFC system designed by waters; **f** Nexera UC Prep preparative SFC system designed by Shimadzu

capillary column SFC processes longer columns that yield more theoretical plate numbers, pack column SFC renewed the interest of researchers due to its more uniform packing materials, smaller diameter, and the ability to pack narrower fused-silica columns compared with open tubular capillary column SFC. The typical packed column SFC system is

developed from HPLC chromatograph by adding photodiode array (PDA) UV detector, pressure transducer, and electronic BPR (Fig. 9b) (Saito 2013).

The typical packed column SFC system is developed from HPLC chromatograph by adding photodiode array (PDA) UV detector, pressure transducer, and electronic

BPR (Fig. 9b) (Saito 2013). During the packed column SFC chromatography process, the pressure transducer can monitor the real-time pressure, which will be compared with the set pressure by BPR. Afterward, by adjusting the flow resistance of the regulator, the actual pressure can maintain equal to the set pressure to keep the stability of chromatography process. Comparing with the open tubular capillary column system, the packed column system can control the pressure independently without the restriction of the mobile phase flow rate. Moreover, Saito et al. (1988) designed a new type of electronically controlled BPR with small volume applied in packed column SFC system, realizing efficient chromatography without cross-contamination between different components. Sugiyama et al. (1985) used the packed column SFC system hyphenated with SFE system to evaluate the extraction and chromatography performance of caffeine from the coffee beans. The SFE system is directly connected to the SFC system, which allowed online introduction to the SFC column, and the PDA is used to monitor the signal. Nowadays, various detectors, e.g., mass spectrometer, can connect online with SFC system.

In the recent years, various key system manufacturers, such as Shimadzu, Jasco, Agilent Technologies, Thar Technologies, Thermo Fisher Scientific, and Waters Corporation, launched their state-of-the-art system, which included both analytical and preparative SFC system.

### Analytical supercritical fluid chromatography

As for the analytical SFC system, SFC-4000 analytical chromatograph designed by Jasco is equipped with a temperature-stabilized pump that can ensure the optimum conditions for pumping liquid CO<sub>2</sub> (Fig. 9c). This system neither requires complicated pretreatment of CO<sub>2</sub>, nor needs a chiller to cool the pump heads. There are also automatic stop-valves for controlling the input and output of CO<sub>2</sub>, as well as the precision BPR for maintaining supercritical conditions with pressure fluctuations. Besides, this system is also equipped with three ovens for different temperature zones, and with one diode array for high-sensitivity component identification and component identification positive confirmation toward enantiomeric separation. These features lead to a significant improvement on the detection performance compared with that from the previous SFC system. Moreover, the ACQUITY Ultra Performance Convergence Chromatograph (UPC<sup>2</sup>) system developed by Waters is improved based on the previous traditional SFC system. In the UPC<sup>2</sup> system, both the CO<sub>2</sub> chilling and compression take place inside a pump with an integrated device. This system also equipped with an active component to further increase the backpressure and with an independent pump heads cooling device achieved by a Peltier module, realizing accurate control of the pressure and temperature,

respectively. The 1260 Infinity II SFC system designed by Agilent Technologies has presented broad power range to support pressure up to 600 bar at flow rates up to 8.3e – 5 L/s for extended application reach and the patented feed injection technology guarantees outstanding injection precision and LC-like reproducibility (Fig. 9d).

### Preparative supercritical fluid chromatography

The successful commercially available preparative SFC system—Prep 150 AP SFC system from Waters offers column switching, automated sample handling, and tracking and fraction collection in an open-bed format (Fig. 9e). This SFC system utilizes scCO<sub>2</sub> as its main mobile phase in combination with one or more organic solvents, which provides routine compound purification with fast separations, high resolution and high throughput for drug discovery labs. The stacked injection capability of system is also available for the purification of large amounts of materials delivered by multiple injections and for allowing for multiple peaks collected into separate vessels. In short, the Prep 150 AP SFC system can provide lower pressure drops across the column, faster equilibration, lower cost per sample, and reduced solvent and thus is reproducible and applicable to a wide range of compounds relevant in the pharmaceutical, food and environmental field, life sciences, and chemical materials. Besides, the semi-preparative SFC system—Nexera UC Prep designed by Shimadzu is equipped with the patented gas–liquid separator (Fig. 9f), which can decrease flow rate without increasing the pipe diameter by splitting flow through multiple channels. CO<sub>2</sub> is discharged externally, while the liquid travels along the column and drips directly into the collection vessel without dispersing or spattering the eluate. These features can successfully reduce sample dispersion and carryover and also achieve high recovery rates, so that the high recovery rates can be obtained regardless of flow rate or modifier concentration, even for volatile compounds such as the fragrance linalool. Nowadays, commercialized analytical and preparative SFC systems are developing rapidly and have been applied for analysis and purification in various fields, and they will attract more and more interests of scientists in future.

Through the introduction of the foregoing, the SFC systems are mainly divided into open tubular capillary column system and packed column system, which all have the common components of CO<sub>2</sub> cylinder, syringe pump, and temperature- and pressure-controlling device, but they present the difference on the reaction column. Moreover, it is worth noting that the SFC systems have been commercialized of both analytical and preparative SFC system.

Overall, SFC has been revived attributed to the introduction of a new generation of columns and instruments from major suppliers of chromatographic instrumentation.



Particularly, using CO<sub>2</sub> as the mobile phase in SFC possesses the advantages of short equilibration time, high flow rate, and low solvent consumption. However, SFC also faces the challenges of high consumption of CO<sub>2</sub>, difficult collection of the solute, and so on. The consumption of CO<sub>2</sub> can be high at high flow rate, such as 3 kg/min for the Supersep 3000 of Novasep supplied by a CO<sub>2</sub> tank, and a B50 cylinder can only supply this system for 11 min. Therefore, recycling and reusing CO<sub>2</sub> by properly tuning the temperature and pressure of CO<sub>2</sub> downstream from the vessel can effectively reduce CO<sub>2</sub> consumption. Consequently, it requires SFC equipped with separate and recovery device to realize good recovery of the solute and pure CO<sub>2</sub> without contamination of CO<sub>2</sub> by the solute and without dissolved solvent inside. The technique designed by Novasep realized the requirement by cleaning the recycled gaseous CO<sub>2</sub> by a flow of liquid CO<sub>2</sub>. Moreover, preparative SFC also face the challenge of the solute collection. The separation of CO<sub>2</sub> and the modifier dissolved the compound inside is realized by depressurizing the mobile phase in downstream of the BPR, which leads to a 500 times higher expansion in the volume. The significant expansion can cause the remixing of the compounds that results in the difference between the final fraction purity and the observation with the UV detector. The volume expansion will also cause aerosol spray leading to low recovery of the solute and contamination in the device. Aiming at the issue, using cyclone at high-pressure for fraction collection realized by the centrifugal force to complete the modifier separation can effectively improve the recovery of the solute, which has been used by some suppliers such as Jasco, Novasep, and Sepiatec. Berger also developed a phase separator to control the depressurization process to collect the modifier under low pressure, during which CO<sub>2</sub> will depressurize from supercritical fluid state to gas state without aerosol formation. The improved SFC with phase separator has been used by Multigram II and Multigram III devices for batch purifications and Autoprep for series of compounds purification. Moreover, Shaimi designed a new process to collect the solute under atmospheric pressure in a series of vessels, which can realize the purification of several compounds consecutively. The process relies on two collection heads, of which one collects the solute and another is flushed by the solvent for cleaning it before collecting the next fraction.

## Cleaning systems

The cleaning of metal devices, optical and laser components, precision mechanical parts, and electronic assemblies for contaminants removal are extremely important and necessary in the manufacturing industry (Meziani et al. 2017). The traditional industrial cleaning mainly uses organic

solvent cleaning and water solution cleaning. The organic solvent cleaning usually employs volatile solvents and halogen-containing chlorofluorocarbons as the solvent, which causes serious damage to the ozone layer and the atmosphere (Allafi et al. 2021). Meanwhile, the water solution cleaning has the problems of complex surfactant accession, long drying time, treated metal easy to rust, secondary pollution, and also inevitably increasing the treatment costs. As an alternative, scCO<sub>2</sub> with low viscosity, zero surface tension, high gas-like diffusivity, and high liquid-like density has becoming an attractive solvent that can be widely used for cleaning of the precision devices (Matz and Reidy 2005). Moreover, scCO<sub>2</sub> can easily reach the hard-to-reach surfaces of the parts with complex geometry and can be absolutely released without any residue. The solvating power of scCO<sub>2</sub> can be adjusted by varying the temperature and pressure as well as adding the cosolvents (Korzynski et al. 2005; Lawandy and Smuk 2014; Weibel and Ober 2003). More importantly, the scCO<sub>2</sub>-assisted cleaning process can be completed simultaneously with drying process, which greatly saves the treatment time and cost in the practical production.

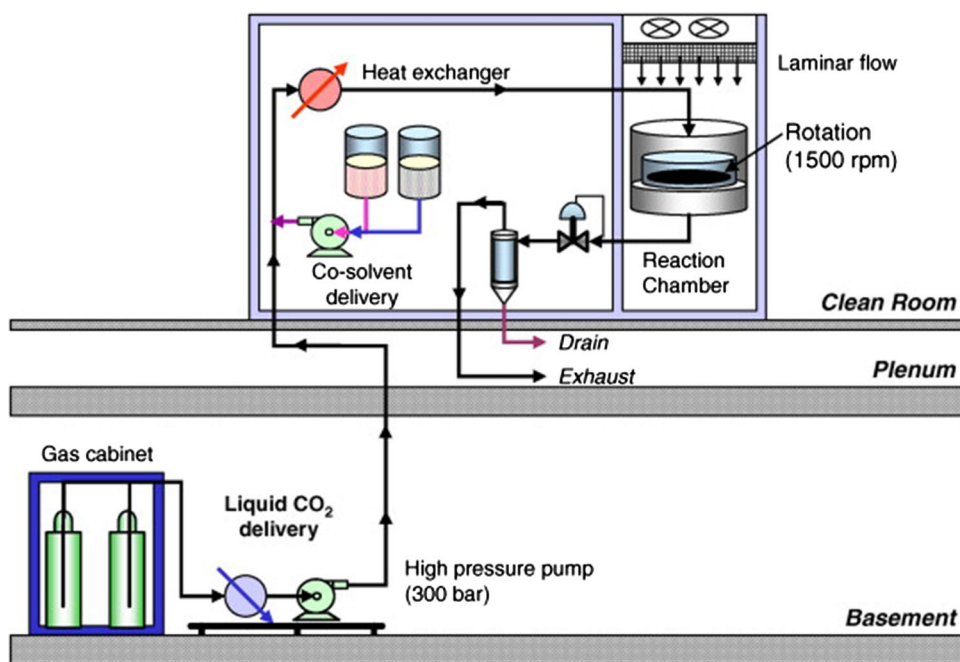
At present, scCO<sub>2</sub> cleaning technology has been applied in several fields, such as precision machinery industry, medical system industry, electronics industry, and optical industry, and therefore, the scCO<sub>2</sub> cleaning systems have also attracted increasing attention. ScCO<sub>2</sub> cleaning systems are designed based on the traditional wet-cleaning systems and employ CO<sub>2</sub> as the cleaning medium to complete the cleaning process under supercritical conditions, and then, the separation of CO<sub>2</sub> and contaminants and the drying of the cleaned samples are realized through decompression process. The critical factors of scCO<sub>2</sub> cleaning systems are reasonable design of the high-pressure cleaning vessel to maintain the contaminants stably dissolves into scCO<sub>2</sub> and not produced repeated pollution due to the parameters fluctuation during the scCO<sub>2</sub> cleaning process, which requires high tightness of the cleaning vessel and precise controlling device of the cleaning conditions. Moreover, ensuring no reattaching of the original dissolved contaminants on the surface of the cleaned samples during the separation and drying process is also important to obtain high cleaning efficiency. In the recent years, scCO<sub>2</sub> cleaning systems at laboratory scale and commercial scale both developed rapidly, which will be introduced separately in the following.

## Laboratory cleaning system

The typical laboratory scCO<sub>2</sub>-assisted cleaning system is shown in Fig. 10 (Ventosa et al. 2008), which consisted of gas cabinet, high-pressure pump, heat exchanger, cosolvent delivery part, and reaction chamber. Ventosa et al. (2008) studied scCO<sub>2</sub>-assisted cleaning for removal of the postetch residues and oxidized copper formed in the post-via after



**Fig. 10** Typical laboratory supercritical carbon dioxide-assisted cleaning system. Reproduced with permission of Elsevier from Ventosa et al. (2008). CO<sub>2</sub> is firstly pumped and pressurized up to the target pressure, and maintained in the process chamber for the residence time. Then, the cosolvent will be pumped and mixed with CO<sub>2</sub> with a fixed proportion, and the mixture will flow into the chamber containing the sample to be cleaned when the mixture reaches the supercritical condition



SiOC-based porous materials etching and photoresist plasma ashing processes by employing this scCO<sub>2</sub>-assisted cleaning system. During the scCO<sub>2</sub>-assisted cleaning process, CO<sub>2</sub> is firstly pumped and pressurized up to the target pressure and maintained in the process chamber for the residence time. Then, the cosolvent will be pumped and mixed with CO<sub>2</sub> with a fixed proportion, and the mixture will flow into the chamber containing the sample to be cleaned when the mixture reaches the supercritical condition. The samples will be continuously rotated with a fixed rotate speed to enhance the mass transfer, thus speeding up the cleaning process. The scCO<sub>2</sub>-assisted cleaning process was divided into two steps, i.e., scCO<sub>2</sub> with cosolvent cleaning process and individual scCO<sub>2</sub> flowing process for removing the cosolvent and drying of the samples. Finally, CO<sub>2</sub> will be released to the room pressure and drove to the exhaust, and the cosolvent will be collected to the vessel. Ito et al. (2004) used the scCO<sub>2</sub>-assisted cleaning system for scCO<sub>2</sub>-assisted cleaning of the air filters and found that the removal efficiency of dioctyl phthalate can highly reached 100%. Wang et al. (1999) explored scCO<sub>2</sub>-assisted cleaning of the residuals of Ni (or Sn/Pb) ions from the surface of electroplated terminations and simultaneously realized batch cleaning and flow cleaning with this scCO<sub>2</sub>-assisted cleaning system by employing the metering valve at the exit of the reaction chamber to control the flow rate of CO<sub>2</sub> and also using a BPR to adjust the pressure to the target level. The results showed that scCO<sub>2</sub>-assisted cleaning ability was superior than that of the deionized water cleaning and found that higher temperature and pressure led to noticeably improved cleaning ability of scCO<sub>2</sub>. Moreover, the scCO<sub>2</sub>-assisted

cleaning ability can be further improved through the agitation by ultrasonic transducers set in the cleaning chamber (Kohli 2015).

Lin et al. (2010) further optimized the typical laboratory scCO<sub>2</sub>-assisted cleaning system by adding the boil-off vessel located downstream from the cleaning vessel and the syringe-type high-pressure pump subsystem. Different from the typical scCO<sub>2</sub>-assisted cleaning process, after the samples soaked and rotated in the scCO<sub>2</sub> and cosolvent mixture under the supercritical condition, CO<sub>2</sub> mixed with contaminants will be flushed out of the cleaning vessel through continuous flow of pure CO<sub>2</sub> in a first-in–first-out (FIFO) process, in which pure CO<sub>2</sub> is pushed by the syringe-type high-pressure pump subsystem at a constant flow rate. The stabilized temperature and pressure in the cleaning vessel during the FIFO flushing and soaking process make the solvent power maintain unchanged, thus minimizing the contamination leftover. After the cleaning process, the contaminants will be left in a filter subsystem. It is worth noting that the decompression process should be slow enough for guaranteeing the temperature in the cleaning vessel will not be too cold due to the Joule–Thomson effect, and the temperature in the boil-off vessel should always maintain slightly higher than the saturated vapor pressure during the decompression process, thus avoiding the bubbles formed that may stir up the contaminants by gravity at the bottom of the cleaning vessel. As a result, most of the bubbles will be formed in the boil-off vessel. Lin et al. (2010) used this improved scCO<sub>2</sub>-assisted cleaning system to study the cleaning ability of the compressed Martian air mix (consisting of 95% CO<sub>2</sub>) under supercritical condition for removing the

trace amounts of microbial and organic contaminants from spacecraft material surfaces. The results demonstrated that scCO<sub>2</sub>-assisted cleaning technology can achieve the cleanliness levels of 0.01 μg/cm<sup>2</sup> or less for the cleaning of hydrophobic contaminants, which shows great potential for future Mars in situ cleaning.

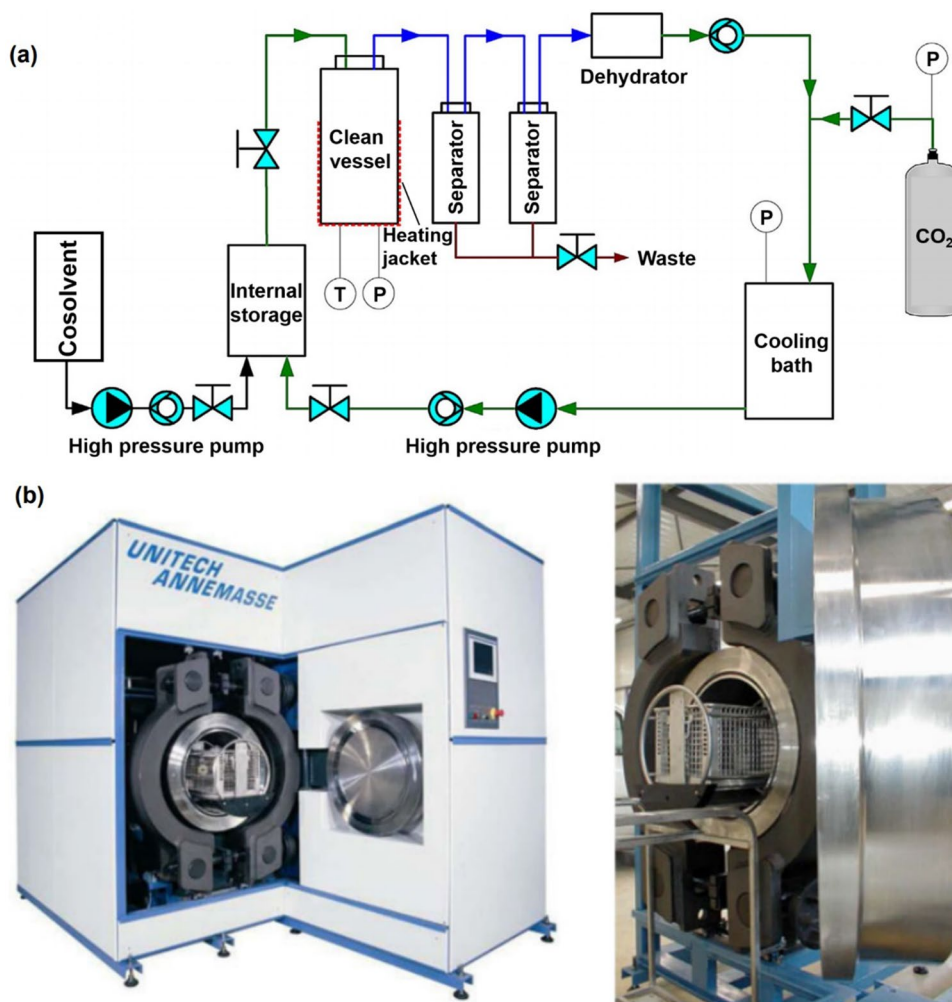
### Commercial cleaning system

With the increasing attractive attention of scCO<sub>2</sub>-assisted cleaning technology, various key system manufacturers launched their commercialized scCO<sub>2</sub>-assisted cleaning systems. The TC-SFE-50-1-120S laboratory scCO<sub>2</sub>-assisted cleaning system manufactured by Suofuer is shown in Fig. 11a (Li et al. 2015; Liu et al. 2014). TC-SFE-50-1-120S laboratory scCO<sub>2</sub>-assisted cleaning system is consisted of a 1-L cylindrical stainless steel cleaning vessel with a length of 360 mm and a diameter of 60 mm, which can be operated at temperatures from 15 to 300 °C and pressures up to 50 MPa. The TC-SFE-50-1-120S laboratory scCO<sub>2</sub>-assisted cleaning system also has two series-wound separators used

for the recovery of the cosolvent, contaminants, and CO<sub>2</sub>. During the scCO<sub>2</sub>-assisted cleaning process, gaseous CO<sub>2</sub> will be transformed into liquid state by condensation and be preheated to the target temperature and then enters the stainless steel cleaning vessel pumped by the high-pressure pump to the pre-set pressure. The temperature in the cleaning vessel is measured by the thermocouple contacted with the fluid inside the vessel to ±2 °C, and the pressure is measured by the piezometer with an accuracy of ±0.2 MPa. The flow rate of CO<sub>2</sub> and pressure in the cleaning vessel can be controlled by both the pump and the heated micro-metering valve. Furtherly, the contaminants in the separator can be recovered, recycled, or reused, if suitable, or the contaminants can be disposed as an individual component without any wastewater, solvents, or other residues that may complicate the subsequent treatment process.

The commercial scCO<sub>2</sub>-assisted cleaning system is shown in Fig. 11b. The commercial scCO<sub>2</sub>-assisted cleaning systems have the low operating and waste disposal costs, but installed costs are from \$100,000 for small-capacity (1-L volume) system to several hundred thousand dollars for

**Fig. 11 a** TC-SFE-50-1-120S laboratory supercritical carbon dioxide (scCO<sub>2</sub>)-assisted cleaning system manufactured by Suofuer. The TC-SFE-50-1-120S laboratory scCO<sub>2</sub>-assisted cleaning system also has two series-wound separators used for the recovery of the cosolvent, contaminants, and CO<sub>2</sub>. Reproduced with permission of Elsevier from Liu et al. (2014), and **b** commercial scCO<sub>2</sub>-assisted cleaning system designed by Unitech-Annemasse



large-capacity (30-L volume) system, and the installed costs increase with the size, the complexity of the components, and the required automation degree. However, the subsequent contaminants treatment cost in the scCO<sub>2</sub>-assisted cleaning process is lower than that of solvent or water solution cleaning technologies, since the waste residue treated by the scCO<sub>2</sub>-assisted cleaning process is 100% contaminant without any other residues or solvents. Consequently, for the contaminants readily soluble in scCO<sub>2</sub>, the scCO<sub>2</sub>-assisted cleaning is undeniably competitive with the solvent or water solution cleaning technologies (Kohli 2015).

Through the introduction of the foregoing, the scCO<sub>2</sub>-assisted cleaning system consists of CO<sub>2</sub> cylinder and pump, cosolvent delivery device, temperature and pressure controller, and the cleaning vessel. Moreover, the scCO<sub>2</sub>-assisted cleaning system can be further improved by employing the separators which are used for the recovery of the cosolvent, contaminants, and CO<sub>2</sub>. The scCO<sub>2</sub>-assisted cleaning system has been commercialized and widely used for the practical industrial cleaning process. ScCO<sub>2</sub>-assisted cleaning technology can meet the contaminants cleaning requirements without compromising the component properties of the devices, and the corresponding scCO<sub>2</sub>-assisted cleaning systems will attract more and more attentions and be applied in practical productions.

Overall, ScCO<sub>2</sub> cleaning technology has been considered a precision cleaning technology applied in many different industries, especially attractive for cleaning intricate parts with complex geometries due to its fascinating properties of gas-like viscosity, liquid-like density, and low surface tension, leading to high wettability. ScCO<sub>2</sub> cleaning system has developed rapidly in both laboratory and industry scale. Nevertheless, ScCO<sub>2</sub> cleaning system also faces several challenges and problems to be solved and further improved for better applying in the practical production. Firstly, when cleaning a large quantity of particulate contaminants in the scCO<sub>2</sub> cleaning system, the blockage can be easily caused at the valves and pipe joints due to the aggregation of particle contaminants, which can lead to local pressure surges in the pipelines and thus result in serious safe problems. Consequently, installing CO<sub>2</sub> flow regulating device to precisely control the CO<sub>2</sub> flow rate and particulate contaminants dissolution in scCO<sub>2</sub> can effectively improve the cleaning efficiency. The second challenge of scCO<sub>2</sub> cleaning system is that when separating scCO<sub>2</sub> and the contaminants by reducing the temperature and pressure after the scCO<sub>2</sub> cleaning process, the solubility of contaminants will decrease due to the transformation of CO<sub>2</sub> from supercritical state to gas state, which may lead to reattaching of the original dissolved contaminants on the surface of the cleaned samples. Aiming at the issue, low-pressure vessel can be added after the high-pressure cleaning vessel for separating CO<sub>2</sub> and the contaminants, while the high-pressure cleaning vessel

can be maintained at constant pressure to avoid reattaching of the contaminants. Moreover, cleaning for large-volume precision instruments still needs to be explored due to the limitations of current volume of the high-pressure cleaning vessel. Developing larger and more flexible scCO<sub>2</sub> cleaning system for cleaning various types of instruments can realize wider applications of scCO<sub>2</sub> cleaning system in the practical industrial production process.

## Perspective

ScCO<sub>2</sub>-based technologies with unique advantages have achieved great achievements for dissolving various types of solutes. Although great progress of scCO<sub>2</sub>-based systems has been made, there are still numerous challenges to be conducted, which also means the valuable directions for future development in both fundamental research and commercial applications of scCO<sub>2</sub>-based systems.

First, the standard of various scCO<sub>2</sub>-based systems for different applications should be more unitized and normalized. The current scCO<sub>2</sub>-based systems for dissolving different types of solutes have similar components composition but present the difference on the reaction vessel due to the specific requirements for dissolving different types of solutes. More unitized and normalized standard of the systems can realize flexible switching of different functions by changing different reaction vessel for dissolving different types of solutes.

Second, the premiumization and intelligentization of scCO<sub>2</sub>-based systems are expected to be realized in future. Most of the current scCO<sub>2</sub>-based systems mainly depend on the manual operation, such as setting the amount of cosolvent, controlling the working conditions, and judging the degree of reaction completion. The manual intervention may influence the accuracy and repeatability of the reaction process, especially under supercritical conditions where minor changes of the temperature/pressure during the reaction process may lead to major variation of the scCO<sub>2</sub> solubility. Therefore, improving the premiumization and intelligentization and reducing the manual intervention of scCO<sub>2</sub>-based systems for more precisely controlling the properties of scCO<sub>2</sub> during the reaction process are in urgent need.

Third, the long-term stability and durability of scCO<sub>2</sub>-based systems should be focused and further improved. The CO<sub>2</sub> compression process usually accompanied with obvious exothermic process, which may affect the normal operation of the CO<sub>2</sub> pressure pump. Meanwhile, the CO<sub>2</sub> decompression process is along with endothermic process, thus leading to freezing around the pipeline, which may cause the blockage in pipelines and the damage of reducing valve. Moreover, the scCO<sub>2</sub>-assisted reactions usually should be maintained at a residence time

under the high-pressure conditions, which greatly requires high air tightness of the reaction vessel. Improving the long-term stability and durability of scCO<sub>2</sub>-based systems can ensure the stability during the reaction process and reduce the system cost.

## Conclusion

Supercritical carbon dioxide (scCO<sub>2</sub>) as a sustainable and efficient solvent has been widely applied for dissolving various types of solutes. This review comprehensively and systematically summarized the sustainable-solvent-scCO<sub>2</sub>-based systems, including dyeing system, extraction system, chromatograph system, and cleaning system, for flexible and efficient dissolution of different types of solutes, i.e., dyes, target solutes in other solvents, component solutes to be separated or purified, and contaminants to be removed, respectively. Based on the detailed introduction of scCO<sub>2</sub>-based systems for dissolving different solutes, it can be found that CO<sub>2</sub> supply and pump part, cosolvent providing part, and parameters controlling part are commonly included in the scCO<sub>2</sub>-based systems. However, the reaction vessel presents difference depending on the specific dissolving requirements and practical functions. Additionally, this review also introduces the difference between the systems, which matched with different production requirements in each application and can be flexibly chosen to apply in the practical production. Through the analysis of the foregoing, focusing and further improving scCO<sub>2</sub>-based systems for flexible and efficient dissolution of various types of solutes based on the application scenarios will render scCO<sub>2</sub>-based technologies be more economic, controllable, flexible, and suitable for wider practical application in future. This review can provide a comprehensive understanding for the construction of scCO<sub>2</sub>-based systems and supply valuable reference for further development and practical industrial applications of scCO<sub>2</sub>-based technologies.

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**Authors' contributions** All authors contributed to the conception and design of this review. XK was involved in conceptualization and writing—original draft. JS was involved in methodology and writing—review and editing. LM, YL, BZ, JX, and YJ were involved in writing—review and revising. EL was involved in writing—review and editing and supervision. HJ was involved in writing—review and editing. LG was involved in supervision and funding acquisition.

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## Declarations

**Conflicts of interest** The authors declare no conflict of interest in this work.

**Ethics approval** EL declares that he is Chief Editor of Environmental Chemistry Letters.

**Consent to participate** Not applicable.

**Consent for publication** Not applicable.

## References

- Abate MT, Ferri A, Guan J, Chen G, Ferreira JA, Nierstrasz V (2019) Single-step disperse dyeing and antimicrobial functionalization of polyester fabric with chitosan and derivative in supercritical carbon dioxide. *J Supercrit Fluids* 147:231–240. <https://doi.org/10.1016/j.supflu.2018.11.002>
- Abate MT, Zhou Y, Guan J, Chen G, Ferri A, Nierstrasz V (2020) Colouration and bio-activation of polyester fabric with curcumin in supercritical CO<sub>2</sub>: part II—effect of dye concentration on the colour and functional properties. *J Supercrit Fluids* 157:104703. <https://doi.org/10.1016/j.supflu.2019.104703>
- Abou ET, Abd EE (2018) Supercritical carbon dioxide as a green media in textile dyeing: a review. *Text Res J* 88:1184–1212. <https://doi.org/10.1177/0040517517697639>
- Abou ET, Abd EE, Ma J, El-Taweel F, Okubayashi S (2015) Eco-friendly disperse dyeing and functional finishing of nylon 6 using supercritical carbon dioxide. *Fibers* 3:309–322. <https://doi.org/10.3390/fib3030309>
- Abou TM, El-Taweel FM, Elsisi HG (2018a) Water-free dyeing of polyester and nylon 6 fabrics with novel 2-oxoacetohydrazonoil cyanide derivatives under a supercritical carbon dioxide medium. *Fibers Polym* 19:887–893. <https://doi.org/10.1007/s12221-018-7766-2>
- Abou ET, El-Taweel F, Elsisi H, Okubayashi S (2018b) Water free dyeing of polypropylene fabric under supercritical carbon dioxide and comparison with its aqueous analogue. *J Supercrit Fluid* 139:114–121. <https://doi.org/10.1016/j.supflu.2018.05.018>
- Abou TM, Sofan M, Kosbar T, Elsisi H, Negm I (2019a) Green approach to dye PET and nylon 6 fabrics with novel pyrazole disperse dyes under supercritical carbon dioxide and its aqueous analogue. *Fibers Polym* 20:2510–2521. <https://doi.org/10.1007/s12221-019-1208-7>
- Abou ET, Kazumasa H, Elsisi H, Mousa A, Sorour H, Gaffer H, Hori T, Hebeish A, Tabata I, Farouk R (2020) Pilot scale water free dyeing of pure cotton under supercritical carbon dioxide. *Carbohydr Polym Technol Appl* 1:100010. <https://doi.org/10.1016/j.carpta.2020.100010>
- Abou ET, Elsisi H, Negm I (2021) Dyeing characteristics of polypropylene fabric dyed with special disperse dyes using supercritical carbon dioxide. *Fiber Polym* 22:1314–1319. <https://doi.org/10.1007/s12221-021-0302-9>
- Abou T, Sofan M, Elsisi H, Kosbar T, Negm E, Hirogaki K, Tabata I, Hori T (2019b) Optimization of an eco-friendly dyeing process in both laboratory scale and pilot scale supercritical carbon dioxide unit for polypropylene fabrics with special new disperse dyes. *J CO<sub>2</sub> Util* 33: 365–371. <https://doi.org/10.1016/j.jcou.2019.06.018>
- Agrawal BJ (2015) Supercritical carbon-dioxide assisted dyeing of textiles: An environmental benign waterless dyeing process. *Int J Innov Res Creat Technol* 1:201–205



- Allafi FAS, Hossain MS, Ab Kadir MO, Shaah MAH, Lalung J, Ahmad MI (2021) Waterless processing of sheep wool fiber in textile industry with supercritical CO<sub>2</sub>: potential and challenges. *J Clean Prod* 285:124819. <https://doi.org/10.1016/j.jclepro.2020.124819>
- Anastas PT (1999) Green chemistry and the role of analytical methodology development. *Crit Rev Anal Chem* 29:167–175. <https://doi.org/10.1080/10408349891199356>
- Anastas P, Eghbali N (2010) Green chemistry: principles and practice. *Chem Soc Rev* 39:301–312. <https://doi.org/10.1039/B918763B>
- Andersen WC, Bruno TJ (2003) Application of a gas–liquid entraining rotor to supercritical fluid extraction: removal of iron (III) from water. *Anal Chim Acta* 485:1–8. [https://doi.org/10.1016/S0003-2670\(03\)00400-8](https://doi.org/10.1016/S0003-2670(03)00400-8)
- Aravindhan R, Monika V, Balamurugan K, Subramanian V, Rao JR, Thanikaivelan P (2017) Highly clean and efficient enzymatic dehairing in green solvents. *J Clean Prod* 140:1578–1586. <https://doi.org/10.1016/j.jclepro.2016.09.211>
- Aslanidou D, Tsiopstias C, Panayiotou C (2013) A novel approach for textile cleaning based on supercritical CO<sub>2</sub> and Pickering emulsions. *J Supercrit Fluid* 76:83–93. <https://doi.org/10.1016/j.supflu.2013.02.005>
- Attard TM, McElroy CR, Gammons RJ, Slattery JM, Supanchaiyamat N, Kamei CLA, Dolstra O, Trindade LM, Bruce NC, McQueen-Mason SJ (2016) Supercritical CO<sub>2</sub> extraction as an effective pretreatment step for wax extraction in a miscanthus biorefinery. *ACS Sustain Chem Eng* 4:5979–5988. <https://doi.org/10.1021/acssuschemeng.6b01220>
- Bai TR, Kobayashi K, Tamura K, Jun Y, Zheng LJ (2019) Supercritical CO<sub>2</sub> dyeing for nylon, acrylic, polyester, and casein buttons and their optimum dyeing conditions by design of experiments. *J CO<sub>2</sub> Util* 33: 253–261. <https://doi.org/10.1016/j.jcou.2019.05.013>
- Banchero M (2013) Supercritical fluid dyeing of synthetic and natural textiles—a review. *Color Technol* 129:2–17. <https://doi.org/10.1111/cote.12005>
- Banchero M (2020) Recent advances in supercritical fluid dyeing. *Color Technol* 136:317–335. <https://doi.org/10.1111/cote.12469>
- Cao J, Su EZ (2021) Hydrophobic deep eutectic solvents: The new generation of green solvents for diversified and colorful applications in green chemistry. *J Clean Prod* 314:127965. <https://doi.org/10.1016/j.jclepro.2021.127965>
- Chassagnez-Mendez AL, Machado NT, Araujo ME, Maia J, Meireles MAA (2000) Supercritical CO<sub>2</sub> extraction of curcumins and essential oil from the rhizomes of turmeric (*Curcuma longa* L.). *Ind Eng Chem Res* 39:4729–4733. <https://doi.org/10.1021/ie000171c>
- Chauvet M, Sauceau M, Fages J (2017) Extrusion assisted by supercritical CO<sub>2</sub>: a review on its application to biopolymers. *J Supercrit Fluid* 120:408–420. <https://doi.org/10.1016/j.supflu.2016.05.043>
- Cornelio-Santiago HP, Gonçalves CB, de Oliveira NA, de Oliveira AL (2017) Supercritical CO<sub>2</sub> extraction of oil from green coffee beans: solubility, triacylglycerol composition, thermophysical properties and thermodynamic modelling. *J Supercrit Fluid* 128:386–394. <https://doi.org/10.1016/j.supflu.2017.05.030>
- Desfontaine V, Guillarme D, Francotte E, Nováková L (2015) Supercritical fluid chromatography in pharmaceutical analysis. *J Pharmaceut Biomed* 113:56–71. <https://doi.org/10.1016/j.jpba.2015.03.007>
- Devi V, Khanam S (2019) Study of ω-6 linoleic and ω-3 α-linolenic acids of hemp (*Cannabis sativa*) seed oil extracted by supercritical CO<sub>2</sub> extraction: CCD optimization. *J Environ Chem Eng* 7:102818. <https://doi.org/10.1016/j.jece.2018.102818>
- Ehlers D, Kirchhoff J, Gerard D, Quirin KW (1998) High-performance liquid chromatography analysis of nutmeg and mace oils produced by supercritical CO<sub>2</sub> extraction—comparison with steam-distilled oils—comparison of East Indian, West Indian and Papuan oils. *Int J Food Sci Tech* 33:215–223. <https://doi.org/10.1046/j.1365-2621.1998.00172.x>
- Fornari T, Vicente G, Vázquez E, García-Risco MR, Reglero G (2012) Isolation of essential oil from different plants and herbs by supercritical fluid extraction. *J Chromatogr A* 1250:34–48. <https://doi.org/10.1016/j.chroma.2012.04.051>
- Friedrich J, Pryde E (1984) Supercritical CO<sub>2</sub> extraction of lipid-bearing materials and characterization of the products. *J Am Oil Chem Soc* 61:223–228. <https://doi.org/10.1007/BF02678773>
- Fujii T, Matsuo Y, Kawasaki S (2018) Rapid continuous supercritical CO<sub>2</sub> extraction and separation of organic compounds from liquid solutions. *Ind Eng Chem Res* 57:5717–5721. <https://doi.org/10.1021/acs.iecr.8b00812>
- Gao D, Yang DF, Cui HS, Huang TT, Lin JX (2015) Supercritical carbon dioxide dyeing for PET and cotton fabric with synthesized dyes by a modified apparatus. *ACS Sustain Chem Eng* 3:668–674. <https://doi.org/10.1021/sc500844d>
- Gao BY, Luo YH, Lu WY, Liu J, Zhang YQ, Yu LL (2017) Triacylglycerol compositions of sunflower, corn and soybean oils examined with supercritical CO<sub>2</sub> ultra-performance convergence chromatography combined with quadrupole time-of-flight mass spectrometry. *Food Chem* 218:569–574. <https://doi.org/10.1016/j.foodchem.2016.09.099>
- Gao ZT, Qu DH, Qu YP, Wang WQ, Cui SR, Guo HX, Li F, Sun FY (2022) A novel jig dyeing apparatus for dyeing polyester with supercritical carbon dioxide and its dyeing effect. *Fiber Polym* 23:745–750. <https://doi.org/10.1007/s12221-022-3314-1>
- Gere DR (1983) Supercritical fluid chromatography. *Science* 222:253–259. <https://doi.org/10.1126/science.6414083>
- Ghoreishi SM, Shahrestani RG, Ghaziaskar HS (2009) Experimental and modeling investigation of supercritical extraction of mannitol from olive leaves. *Chem Eng Technol* 32:45–54. <https://doi.org/10.1002/ceat.200800441>
- Goñi ML, Gañán NA, Martini RE (2021) Supercritical CO<sub>2</sub>-assisted dyeing and functionalization of polymeric materials: a review of recent advances (2015–2020). *J CO<sub>2</sub> Util* 54: 101760. <https://doi.org/10.1016/j.jcou.2021.101760>
- Güçlü-Üstündağ Ö, Temelli F (2005) Solubility behavior of ternary systems of lipids, cosolvents and supercritical carbon dioxide and processing aspects. *J Supercrit Fluid* 36:1–15. <https://doi.org/10.1016/j.supflu.2005.03.002>
- Györi E, Varga A, Fábrián I, Lázár I (2019) Supercritical CO<sub>2</sub> extraction and selective adsorption of aroma materials of selected spice plants in functionalized silica aerogels. *J Supercrit Fluid* 148:16–23. <https://doi.org/10.1016/j.supflu.2019.02.025>
- Hawthorne SB, Miller DJ (1986) Extraction and recovery of organic pollutants from environmental solids and Tenax-GC using supercritical CO<sub>2</sub>. *J Chromatogr Sci* 24:258–264. <https://doi.org/10.1093/chromsci/24.6.258>
- He M, Hong L, Yang ZY, Yang TB, Zeng J (2018) Bioactive assay and hyphenated chromatography detection for complex supercritical CO<sub>2</sub> extract from Chaihu Shugan San using an experimental design approach. *Microchem J* 142:394–402. <https://doi.org/10.1016/j.microc.2018.07.016>
- Heiland JJ, Geissler D, Piendl SK, Warias R, Belder D (2019) Supercritical-fluid chromatography on-chip with two-photon-excited-fluorescence detection for high-speed chiral separations. *Anal Chem* 91:6134–6140. <https://doi.org/10.1021/acs.analchem.9b00726>
- Herrero M, Mendiola JA, Cifuentes A, Ibáñez E (2010) Supercritical fluid extraction: recent advances and applications. *J Chromatogr A* 1217:2495–2511. <https://doi.org/10.1016/j.chroma.2009.12.019>
- Huang T, Cui H, Yang D, Kong X, Lin J (2017) Continuous dyeing processes for zipper tape in supercritical carbon dioxide. *J Clean Prod* 158:95–100. <https://doi.org/10.1016/j.jclepro.2017.04.167>



- Huang T, Kong X, Cui H, Zhang T, Li W, Yu P, Lin J (2019) Waterless dyeing of zipper tape using pilot-scale horizontal supercritical carbon dioxide equipment and its green and efficient production. *J Clean Prod* 233:1097–1105. <https://doi.org/10.1016/j.jclepro.2019.06.189>
- Ito T, Otani Y, Inomata H (2004) Performance of air filters cleaned by supercritical carbon dioxide. *Sep Purif Technol* 40:41–46. <https://doi.org/10.1016/j.seppur.2004.01.002>
- Järvenpää EP, Jestoi MN, Huopalahti R (1997) Quantitative determination of phototoxic furocoumarins in celeriac (*Apium graveolens* L. var. *rapeceum*) using supercritical fluid extraction and high performance liquid chromatography. *Phytochem Anal* 8:250–256. [https://doi.org/10.1002/\(SICI\)1099-1565\(199709/10\)8:5%3c250::AID-PCA368%3e3.3.CO;2-L](https://doi.org/10.1002/(SICI)1099-1565(199709/10)8:5%3c250::AID-PCA368%3e3.3.CO;2-L)
- Jaxel J, Liebner FW, Hansmann C (2020) Solvent-free dyeing of solid wood in water-saturated supercritical carbon dioxide. *ACS Sustain Chem Eng* 8:5446–5451. <https://doi.org/10.1021/acssuschemeng.0c01273>
- Kang JH, Wan R, Zhou FB, Liu YK, Li ZQ, Yin YS (2020) Effects of supercritical CO<sub>2</sub> extraction on adsorption characteristics of methane on different types of coals. *Chem Eng J* 388:123449. <https://doi.org/10.1016/j.cej.2019.123449>
- Kazarian SG, Brantley NH, West BL, Vincent MF, Eckert CA (1997) In situ spectroscopy of polymers subjected to supercritical CO<sub>2</sub>: plasticization and dye impregnation. *Appl Spectrosc* 51:491–494. <https://doi.org/10.1366/0003702971940765>
- Khaw KY, Parat MO, Shaw PN, Nguyen TT, Pandey S, Thurecht KJ, Falconer JR (2019) Factorial design-assisted supercritical carbon-dioxide extraction of cytotoxic active principles from carica papaya leaf juice. *Sci Rep-UK* 9:1716. <https://doi.org/10.1038/s41598-018-37171-9>
- Kim T, Park G, Kong W, Lee YW (2018) Supercritical dyeing technology. *Clean Technol* 24:1–8. <https://doi.org/10.7464/ksct.2018.24.1.001>
- Kitada K, Machmudah S, Sasaki M, Goto M, Nakashima Y, Kumamoto S, Hasegawa T (2009) Supercritical CO<sub>2</sub> extraction of pigment components with pharmaceutical importance from *Chlorella vulgaris*. *J Chem Technol Biot* 84:657–661. <https://doi.org/10.1002/jctb.2096>
- Kohli R (2015) *Supercritical carbon dioxide cleaning: Relevance to particle removal. Particle adhesion and removal*. Wiley, Hoboken, pp 477–518
- Korzenski MB, Bernhard D, Baum T, Saga K, Kuniyasu H, Hattori T (2005) Chemical additive formulations for particle removal in SCCO<sub>2</sub>-based cleaning. *Solid State Phenom* 103–104:193–198. <https://doi.org/10.4028/www.scientific.net/SSP.103-104.193>
- Laroze LE, Díaz-Reinoso B, Moure A, Zúñiga ME, Domínguez H (2010) Extraction of antioxidants from several berries pressing wastes using conventional and supercritical solvents. *Eur Food Res Technol* 231:669–677. <https://doi.org/10.1007/s00217-010-1320-9>
- Lawandy NM, Smuk AY (2014) Supercritical fluid cleaning of banknotes. *Ind Eng Chem Res* 53:530–540. <https://doi.org/10.1021/ie403307y>
- Lazze MC, Pizzala R, Gutierrez Pecharrroman FJ, Gatón Garnica P, Antolin Rodríguez JM, Fabris N, Bianchi L (2009) Grape waste extract obtained by supercritical fluid extraction contains bioactive antioxidant molecules and induces antiproliferative. *J Med Food* 12:561–568. <https://doi.org/10.1089/jmf.2008.0150>
- Lebedev A, Katalevich A, Menshutina N (2015) Modeling and scale-up of supercritical fluid processes. Part I: supercritical drying. *J Supercrit Fluid* 106:122–132. <https://doi.org/10.1016/j.supflu.2015.06.010>
- Li Q, Zhang Z, Zhong C, Liu Y, Zhou Q (2003) Solubility of solid solutes in supercritical carbon dioxide with and without cosolvents. *Fluid Phase Equilib* 207:183–192. [https://doi.org/10.1016/S0378-3812\(03\)00022-0](https://doi.org/10.1016/S0378-3812(03)00022-0)
- Li MZ, Liu WW, Short T, Qing XC, Dong YZ, He YM, Zhang HC (2015) Pre-treatment of remanufacturing cleaning by use of supercritical CO<sub>2</sub> in comparison with thermal cleaning. *Clean Technol Environ* 17:1563–1572. <https://doi.org/10.1007/s10098-014-0888-3>
- Lin Y, Zhong F, Aveline D, Anderson M, Chung S, Mennella J, Schubert W (2010) Supercritical CO<sub>2</sub> cleaning for planetary protection and contamination control. 2010 IEEE aerospace conference, Montana. <https://doi.org/10.1109/AERO.2010.5446981>
- Liu ZT, Zhang L, Liu Z, Gao Z, Dong W, Xiong H, Peng Y, Tang S (2006) Supercritical CO<sub>2</sub> dyeing of ramie fiber with disperse dye. *Ind Eng Chem Res* 45:8932–8938. <https://doi.org/10.1021/ie061093h>
- Liu G, Xu X, Hao Q, Gao Y (2009) Supercritical CO<sub>2</sub> extraction optimization of pomegranate (*Punica granatum* L.) seed oil using response surface methodology. *LWT Food Sci Technol* 42:1491–1495. <https://doi.org/10.1016/j.lwt.2009.04.011>
- Liu WW, Zhang B, Li YZ, He YM, Zhang HC (2014) An environmentally friendly approach for contaminants removal using supercritical CO<sub>2</sub> for remanufacturing industry. *Appl Surf Sci* 292:142–148. <https://doi.org/10.1016/j.apsusc.2013.11.102>
- Liu M, Zhao H, Wu J, Xiong X, Zheng L (2018) Eco-friendly curcumin-based dyes for supercritical carbon dioxide natural fabric dyeing. *J Clean Prod* 197:1262–1267. <https://doi.org/10.1016/j.jclepro.2018.06.202>
- Lu HM, Ni WD, Liang YZ, Man RL (2006) Supercritical CO<sub>2</sub> extraction of emodin and physcion from *Polygonum cuspidatum* and subsequent isolation by semipreparative chromatography. *J Sep Sci* 29:2136–2142. <https://doi.org/10.1002/jssc.200600012>
- Machado BAS, Pereira CG, Nunes SB, Padilha FF, Umsza-Guez MA (2013) Supercritical fluid extraction using CO<sub>2</sub>: main applications and future perspectives. *Sep Sci Technol* 48:2741–2760. <https://doi.org/10.1080/01496395.2013.811422>
- Matz P, Reidy R (2005) Supercritical CO<sub>2</sub> applications in BEOL cleaning. *Solid State Phenom* 103–104:315–322. <https://doi.org/10.4028/www.scientific.net/SSP.103-104.315>
- Medina-Gonzalez Y, Camy S, Condoret JS (2014) ScCO<sub>2</sub>/green solvents: biphasic promising systems for cleaner chemicals manufacturing. *ACS Sustain Chem Eng* 2:2623–2636. <https://doi.org/10.1021/sc5004314>
- Meziani MJ, Pathak P, Sun YP (2017) *Supercritical carbon dioxide in semiconductor cleaning. Handbook of semiconductor manufacturing technology*. CRC Press, Boca Raton, pp 6–28
- Mo SY, Mo MN, He JC (2020) Investigation on the method of sizing and desizing for supercritical carbon dioxide anhydrous dyeing and related equipment. *Dye Finish Technol* 5:65–68. <https://doi.org/10.16481/j.cnki.ctl.2020.05.015>
- Mohammad A, Inamuddin D (2012) *Green solvents II: properties and applications of ionic liquids*. Springer, Dordrecht
- Mouahid A, Crampon C, Toudji SAA, Badens E (2013) Supercritical CO<sub>2</sub> extraction of neutral lipids from microalgae: experiments and modelling. *J Supercrit Fluid* 77:7–16. <https://doi.org/10.1016/j.supflu.2013.01.024>
- Naikoo GA, Saedi ZM, Zamani PM, Hassan IU, Ahmed W, Yousefi AG (2021) Solubility of vitamin A in supercritical CO<sub>2</sub>: experimental study and thermodynamic modeling. *Sci Rep-UK* 11:1–13. <https://doi.org/10.1007/s10098-014-0888-3>
- Pacheco-Fernández I, Pino V (2019) Green solvents in analytical chemistry. *Curr Opin Green Sust* 18:42–50. <https://doi.org/10.1016/j.cogsc.2018.12.010>
- Patil PD, Dandamudi KPR, Wang J, Deng Q, Deng S (2018) Extraction of bio-oils from algae with supercritical carbon dioxide and cosolvents. *J Supercrit Fluid* 135:60–68. <https://doi.org/10.1016/j.supflu.2017.12.019>

- Penthala R, Kumar RS, Heo G, Kim H, Lee IY, Ko EH, Son YA (2019) Synthesis and efficient dyeing of anthraquinone derivatives on polyester fabric with supercritical carbon dioxide. *Dyes Pigments* 166:330–339. <https://doi.org/10.1016/j.dyepig.2019.03.027>
- Penthala R, Heo G, Kim H, Lee IY, Ko EH, Son YA (2020) Synthesis of azo and anthraquinone dyes and dyeing of nylon-6, 6 in supercritical carbon dioxide. *J CO<sub>2</sub> Util* 38: 49–58. <https://doi.org/10.1016/j.jcou.2020.01.013>
- Planeta J, Roth M (2004) Partition coefficients of low-volatility solutes in the ionic liquid 1-n-butyl-3-methylimidazolium hexafluorophosphate–supercritical CO<sub>2</sub> system from chromatographic retention measurements. *J Phys Chem B* 108:11244–11249. <https://doi.org/10.1021/jp049094f>
- Pradhan RC, Meda V, Rout PK, Naik S, Dalai AK (2010) Supercritical CO<sub>2</sub> extraction of fatty oil from flaxseed and comparison with screw press expression and solvent extraction processes. *J Food Eng* 98:393–397. <https://doi.org/10.1016/j.jfoodeng.2009.11.021>
- Pyo D (2001) New device for controlling the amount of methanol in carbon dioxide mobile phase for supercritical fluid chromatography. *Microchem J* 68:183–188. [https://doi.org/10.1016/S0026-265X\(00\)00153-3](https://doi.org/10.1016/S0026-265X(00)00153-3)
- Pyo DN, Lee SY (1999) Addition of water in carbon dioxide mobile phase for supercritical fluid chromatography. *B Korean Chem Soc* 20:405–407. <https://doi.org/10.1039/an9931800253>
- Qamar S, Manrique YJ, Parekh HS, Falconer JR (2021) Development and optimization of supercritical fluid extraction setup leading to quantification of 11 cannabinoids derived from medicinal cannabis. *Biology* 10:481. <https://doi.org/10.3390/biology10060481>
- Qi HB, Gui N, Yang XT, Tu JY, Jiang SY (2018) The application of supercritical CO<sub>2</sub> in nuclear engineering: a review. *J Comput Multiphas Flow* 10:149–158. <https://doi.org/10.1177/1757482X18765377>
- Ramsey E, Sun QB, Zhang ZQ, Zhang CM, Gou W (2009) Mini-review: green sustainable processes using supercritical fluid carbon dioxide. *J Environ Sci* 21:720–726. [https://doi.org/10.1016/S1001-0742\(08\)62330-X](https://doi.org/10.1016/S1001-0742(08)62330-X)
- Reji R, Raman S, Kim T, Kim H (2019) Computational fluid dynamics simulation of the supercritical carbon dioxide flow in beam dyeing. *Text Res J* 89:2604–2615. <https://doi.org/10.1177/0040517518798647>
- Reverchon E, Senatore F (1992) Isolation of rosemary oil: comparison between hydrodistillation and supercritical CO<sub>2</sub> extraction. *Flavour Frag J* 7:227–230. <https://doi.org/10.1002/ffj.2730070411>
- Rezaei K, Temelli F (2000) Using supercritical fluid chromatography to determine diffusion coefficients of lipids in supercritical CO<sub>2</sub>. *J Supercrit Fluid* 17:35–44. [https://doi.org/10.1016/S0896-8446\(99\)00039-X](https://doi.org/10.1016/S0896-8446(99)00039-X)
- Rochfort S, Isbel A, Ezernieks V, Elkins A, Vincent D, Deseo MA, Spangenberg GC (2020) Utilisation of design of experiments approach to optimise supercritical fluid extraction of medicinal cannabis. *Sci Rep-UK* 10:1–7. <https://doi.org/10.1038/s41598-020-66119-1>
- Sabio E, Lozano M, Espinosa VM, Mendes RL, Pereira AP, Palavra AF, Coelho JA (2003) Lycopene and  $\beta$ -carotene extraction from tomato processing waste using supercritical CO<sub>2</sub>. *Ind Eng Chem Res* 42:6641–6646. <https://doi.org/10.1021/ie0301233>
- Sahena F, Zaidul I, Jinap S, Karim A, Abbas K, Norulaini N, Omar A (2009) Application of supercritical CO<sub>2</sub> in lipid extraction—a review. *J Food Eng* 95:240–253. <https://doi.org/10.1016/j.jfoodeng.2009.06.026>
- Saito M (2013) History of supercritical fluid chromatography: instrumental development. *J Biosci Bioeng* 115:590–599. <https://doi.org/10.1016/j.jbiosc.2012.12.008>
- Saito M, Yamauchi Y, Kashiwazaki H, Sugawara M (1988) New pressure regulating system for constant mass flow supercritical-fluid chromatography and physico-chemical analysis of mass-flow reduction in pressure programming by analogous circuit model. *Chromatographia* 25:801–805. <https://doi.org/10.1007/BF02262088>
- Salgın U, Döker O, Çalimli A (2006) Extraction of sunflower oil with supercritical CO<sub>2</sub>: experiments and modeling. *J Supercrit Fluid* 38:326–331. <https://doi.org/10.1016/j.supflu.2005.11.015>
- Cheng C, Mao LH, Kang X, Dong CL, Huang YC, Shen SH, Shi JW, Guo LJ (2023) A high-cyano groups-content amorphous-crystalline carbon nitride isotype heterojunction photocatalyst for high-quantum-yield H<sub>2</sub> production and enhanced CO<sub>2</sub> reduction. *Appl Catal B-Environ* 331:122733. <https://doi.org/10.1016/j.apcatb.2023.122733>
- Saus W, Knittel D, Schollmeyer E (1993) Dyeing of textiles in supercritical carbon dioxide. *Text Res J* 63:135–142. <https://doi.org/10.1177/004051759306300302>
- Sharif K, Rahman M, Azmir J, Mohamed A, Jahurul M, Sahena F, Zaidul I (2014) Experimental design of supercritical fluid extraction—a review. *J Food Eng* 124:105–116. <https://doi.org/10.1016/j.jfoodeng.2013.10.003>
- Sihvonen M, Järvenpää E, Hietaniemi V, Huopalahti R (1999) Advances in supercritical carbon dioxide technologies. *Trends Food Sci Tech* 10:217–222. [https://doi.org/10.1016/S0924-2244\(99\)00049-7](https://doi.org/10.1016/S0924-2244(99)00049-7)
- Silva W, Romero J, Morales E, Melo R, Mendoza L, Cotoras M (2017) Red wine extract obtained by membrane-based supercritical fluid extraction: preliminary characterization of chemical properties. *Braz J Chem Eng* 34:567–581. <https://doi.org/10.1590/0104-6632.20170342s20150631>
- Soh SH, Agarwal S, Jain A, Lee LY, Chin SK, Jayaraman S (2019) Mathematical modeling of mass transfer in supercritical fluid extraction of patchouli oil. *Eng Rep* 1:e12051. <https://doi.org/10.1002/eng2.12051>
- Spanos GA, Chen H, Schwartz SJ (1993) Supercritical CO<sub>2</sub> extraction of  $\beta$ -carotene from sweet potatoes. *J Food Sci* 58(4):817–820. <https://doi.org/10.1111/j.1365-2621.1993.tb09366.x>
- Speybrouck D, Lipka E (2016) Preparative supercritical fluid chromatography: a powerful tool for chiral separations. *J Chromatogr A* 1467:33–55. <https://doi.org/10.1016/j.chroma.2016.07.050>
- Srinivas D, Harish N, Kumar KA, Kumar S (2017) Process parameters affecting the supercritical fluid extraction—a review. *Int J Agric Sci Res* 7:617–624. <https://doi.org/10.24247/ijasraug201780>
- Sugiyama K, Saito M, Hondo T, Senda M (1985) New double-stage separation analysis method: directly coupled laboratory-scale supercritical fluid extraction—supercritical fluid chromatography, monitored with a multiwavelength ultraviolet detector. *J Chromatogr A* 332:107–116. [https://doi.org/10.1016/S0021-9673\(01\)83289-1](https://doi.org/10.1016/S0021-9673(01)83289-1)
- Sun M, Temelli F (2006) Supercritical carbon dioxide extraction of carotenoids from carrot using canola oil as a continuous cosolvent. *J Supercrit Fluid* 37:397–408. <https://doi.org/10.1016/j.supflu.2006.01.008>
- Tavares MCH, Lanças FM (2000) Open tubular supercritical fluid chromatography (ot-SFC) applied to the separation of coal-derived products obtained by supercritical fluid extraction (SFE). *J High Res Chrom* 23:515–518. [https://doi.org/10.1002/1521-4168\(20000801\)23:7/8%3e515::AID-JHRC515%3e3.0.CO;2-R](https://doi.org/10.1002/1521-4168(20000801)23:7/8%3e515::AID-JHRC515%3e3.0.CO;2-R)
- Taylor LT (2009) Supercritical fluid chromatography for the 21st century. *J Supercrit Fluid* 47:566–573. <https://doi.org/10.1016/j.supflu.2008.09.012>
- Ting SS, Tomasko DL, Foster NR, Macnaughton SJ (1993) Solubility of naproxen in supercritical carbon dioxide with and without cosolvents. *Ind Eng Chem Res* 32:1471–1481. <https://doi.org/10.1021/ie00019a022>
- Topal U, Sasaki M, Goto M, Hayakawa K (2006) Extraction of lycopene from tomato skin with supercritical carbon dioxide: effect of

- operating conditions and solubility analysis. *J Agric Food Chem* 54:5604–5610. <https://doi.org/10.1021/jf0606407>
- Tyśkiewicz K, Gieysztor R, Konkol M, Szafas J, Rójs E (2018) Essential oils from *Humulus lupulus* scCO<sub>2</sub> extract by hydrodistillation and microwave-assisted hydrodistillation. *Molecules* 23:2866. <https://doi.org/10.3390/molecules23112866>
- Vági E, Simándi B, Vásárhelyiné KP, Daood H, Kéry Á, Doleschall F, Nagy B (2007) Supercritical carbon dioxide extraction of carotenoids, tocopherols and sitosterols from industrial tomato by-products. *J Supercrit Fluid* 40:218–226. <https://doi.org/10.1016/j.supflu.2006.05.009>
- Van Zelst F, van Meerten S, van Bentum P, Kentgens A (2018) Hyphenation of supercritical fluid chromatography and NMR with in-line sample concentration. *Anal Chem* 90:10457–10464. <https://doi.org/10.1021/acs.analchem.8b02357>
- Ventosa C, Rébiscoul D, Perrut V, Ivanova V, Renault O, Passemard G (2008) Copper cleaning in supercritical CO<sub>2</sub> for the microprocessor interconnects. *Microelectron Eng* 85:1629–1638. <https://doi.org/10.1016/j.mee.2008.03.018>
- Vladić J, Duarte ARC, Radman S, Simić S, Jerković I (2021) Enzymatic and microwave pretreatments and supercritical CO<sub>2</sub> extraction for improving extraction efficiency and quality of *Origanum vulgare* L. spp. hirtum extracts. *Plants* 11:54. <https://doi.org/10.3390/plants11010054>
- Wang ML, Wang WQ (2014) Study on the strength of textile during the process of supercritical fluids spray dyeing. *Adv Mater Res* 951:41–44. <https://doi.org/10.4028/www.scientific.net/AMR.951.41>
- Wang CW, Chang RT, Lin WK, Lin RD, Liang MT, Yang JF, Wang JB (1999) Supercritical CO<sub>2</sub> fluid for chip resistor cleaning. *J Electrochem Soc* 146:3485. <https://doi.org/10.1149/1.1392501>
- Wang ML, Wang WQ, Qu YP, Liu Y, Xu ZY (2012) Supercritical fluid spray dyeing: a new method of dyeing and simulations of its flow field. *Adv Mater Res* 396–398:2038–2043. <https://doi.org/10.4028/www.scientific.net/AMR.396-398.2038>
- Weibel GL, Ober CK (2003) An overview of supercritical CO<sub>2</sub> applications in microelectronics processing. *Microelectron Eng* 65:145–152. [https://doi.org/10.1016/S0167-9317\(02\)00747-5](https://doi.org/10.1016/S0167-9317(02)00747-5)
- Xiong X, Xu Y, Zheng L, Yan J, Zhao H, Zhang J, Sun Y (2017) Polyester fabric's fluorescent dyeing in supercritical carbon dioxide and its fluorescence imaging. *J Fluoresc* 27:483–489. <https://doi.org/10.1007/s10895-016-1975-0>
- Yan K, Zhang Y, Xiao H, Shi M, Long J (2020) Development of a special SCFX-AnB<sub>3</sub>L dye and its application in ecological dyeing of silk with supercritical carbon dioxide. *J CO<sub>2</sub> Util* 35: 67–78. <https://doi.org/10.1016/j.jcou.2019.09.004>
- Yang MY, Liu J, Zhang YQ, Chen C, Wang K, Peng C, Long JJ (2014) Rope dyeing of fabric in supercritical carbon dioxide for commercial purposes. *Color Technol* 130:102–111. <https://doi.org/10.1111/cote.12076>
- Yang DF, Kong XJ, Gao D, Cui HS, Huang TT, Lin JX (2017) Dyeing of cotton fabric with reactive disperse dye contain acyl fluoride group in supercritical carbon dioxide. *Dyes Pigment* 139:566–574. <https://doi.org/10.1016/j.dyepig.2016.12.050>
- Yu J, Dandekar DV, Toledo RT, Singh RK, Patil BS (2007) Supercritical fluid extraction of limonoids and naringin from grapefruit (*Citrus paradisi* Macf.) seeds. *Food Chem* 105:1026–1031. <https://doi.org/10.1016/j.foodchem.2007.04.062>
- Zhang Y, Wei X, Long J (2016) Ecofriendly synthesis and application of special disperse reactive dyes in waterless coloration of wool with supercritical carbon dioxide. *J Clean Prod* 133:746–756. <https://doi.org/10.1016/j.jclepro.2016.05.187>
- Zhang J, Zheng LJ, Su YH, Liu M, Yan J, Xiong XQ (2017) Dyeing behavior prediction of cotton fabrics in supercritical CO<sub>2</sub>. *Therm Sci* 21:1739–1744. <https://doi.org/10.2298/TSCI160805062Z>
- Zhang Z, Sun FY, Li QL, Wang WQ, Hu DD, Li SC (2020) Establishment of the predicting models of the dyeing effect in supercritical carbon dioxide based on the generalized regression neural network and back propagation neural network. *Processes* 8:1631. <https://doi.org/10.3390/pr8121631>
- Zheng LJ, Zheng HD, Du B, Wei J, Gao SH, Zhang J (2015a) Dyeing procedures of polyester fiber in supercritical carbon dioxide using a special dyeing frame. *J Eng Fiber Fabr* 10:155892501501000420. <https://doi.org/10.1177/155892501501000414>
- Zheng LJ, Yin PP, Ye F, Wei J, Yan J (2015b) Effect of pressure of supercritical carbon dioxide on morphology of wool fibers during dyeing process. *Therm Sci* 19:1297–1300. <https://doi.org/10.2298/TSCI1504297Z>
- Zheng HD, Xu YY, Zhang J, Xiong XQ, Yan J, Zheng LJ (2017a) An ecofriendly dyeing of wool with supercritical carbon dioxide fluid. *J Clean Prod* 143:269–277. <https://doi.org/10.1016/j.jclepro.2016.12.115>
- Zheng GD, Liu MS, Chao YX, Yang YH, Zhang DD, Tao YW, Zhang JY, Zeng CF, Wei MY (2020) Identification of lipophilic components in *Citri Reticulatae* Pericarpium cultivars by supercritical CO<sub>2</sub> fluid extraction with ultra-high-performance liquid chromatography–Q Exactive Orbitrap tandem mass spectrometry. *J Sep Sci* 43:3421–3440. <https://doi.org/10.1002/jssc.202000490>
- Zheng HD, Zhang J, Yan J, Zheng LJ (2016) An industrial scale multiple supercritical carbon dioxide apparatus and its eco-friendly dyeing production. *J CO<sub>2</sub> Util* 16: 272–281. <https://doi.org/10.1016/j.jcou.2016.08.002>
- Zheng H, Zhang J, Liu M, Yan J, Zhao H, Zheng L (2017b) CO<sub>2</sub> Utilization for the dyeing of yak hair: Fracture behaviour in supercritical state. *J CO<sub>2</sub> Util* 18: 117–124. <https://doi.org/10.1016/j.jcou.2017.01.008>
- Zhou Y, Lima TA, Hinton ZR, Henry CK, Anand M, Alvarez NJ (2023) A novel scCO<sub>2</sub> dyeing strategy for superior coloration of UHMWPE fiber. *Polymer* 273:125873. <https://doi.org/10.1016/j.polymer.2023.125873>
- Zougagh M, Valcárcel M, Ríos A (2004) Supercritical fluid extraction: a critical review of its analytical usefulness. *Trac-Trend Anal Chem* 23:399–405. [https://doi.org/10.1016/S0165-9936\(04\)00524-2](https://doi.org/10.1016/S0165-9936(04)00524-2)
- Zulkafli ZD, Wang H, Miyashita F, Utsumi N, Tamura K (2014) Cosolvent-modified supercritical carbon dioxide extraction of phenolic compounds from bamboo leaves (*Sasa palmata*). *J Supercrit Fluid* 94:123–129. <https://doi.org/10.1016/j.supflu.2014.07.008>

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