Review

Decontamination of hazardous substances from solid matrices and liquids using supercritical fluids extraction: A review

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ABSTRACT

Supercritical fluid has been adopted as an extraction media to remove various kinds of substances from distinct types of solid matrices since three decades ago. Compared to conventional extraction mode, supercritical fluid extraction technology is preferred because of the flexibility in adjusting its dissolving power and inherent elimination of organic solvent which means reducing time and money needed for subsequent purification. Utilization of this method as an environmental remedial technology, however, has become a trend only after its accomplishment in analytical chemistry was acknowledged. This review tries to summarize in a comprehensive manner the multitude aspects involved in hazardous compounds removal from miscellaneous class of environmental matrices. The industrial adsorbent regeneration using supercritical fluid technology is also discussed. Although, this technology has been successfully realized for environmental remediation in laboratory and on pilot-plant scale, its commercialization attempts still lack significant technology improvement in order to reach the economic feasibility.

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Contents

1. Introduction

In the ever-growing trend of environmental-concerned society, it is apparent that many countries are starting to apply strict environmental regulations in almost every aspect associated with human life. Clean technology such as supercritical extraction has become a back-bone of the major policies worldwide mainly utilized for the end of pipe treatment as well as for analysis, processing and quality control. The pristine application of the supercritical extraction technology was for the recovery of various compounds from distinct natural resources or environmental purpose and till present time this area is still widely studied [1]. Comprehensive

Nomenclature

a	pure component parameter (Eq. (2))
b	a specific constant (Eq. (2))
a', b'	parameters (Eq. (5))
a_{ij}, b_{ij}	cross coefficients (Eqs. (3) and (4))
c	concentration of solute in gas (Eq. (5))
C	extract concentration in fluid phase (Eqs. (16)–(18) and (21))
C_e^*	equilibrium concentration in supercritical fluid (Eqs. (13) and (14))
C_s, C_i	concentration of adsorbed solute and solute in the pores (Eq. (12))
C_a, C_i, C_m	adsorbed concentration, concentration in pore and monolayer adsorbed concentration (Eqs. (21)–(23))
d	density of gas (Eq. (5))
D_e	effective diffusivity in the porous particle (Eq. (22))
E	an enhancement factor (Eqs. (8) and (9))
E'	a characteristic energy (Eq. (15))
F	fraction of analyte released quickly (Eq. (25))
g, h	constants (Eq. (7))
ΔH_{fus}^m	enthalpy of fusion for solute in (Eq. (10))
k	an association number (Eq. (5))
k_a'	adsorption rate constant (Eq. (12))
k_a	a second-order adsorption rate constant (Eqs. (22) and (23))
k_d	desorption rate constant (Eq. (19))
k_m	mass transfer coefficient (Eq. (21))
k_1	first-order rate constant describing quickly release fraction (Eq. (25))
k_2	first-order rate constant describing slowly release fraction (Eq. (25))
K	adsorption equilibrium constant (Eq. (12))
K'	equilibrium adsorption coefficient (Eq. (13))
P	pressure
P_{ref}	standard pressure of 1 bar (Eq. (6))
P', P_s	pressure at equilibrium and saturation (Eq. (15))
q	extract concentration in solid phase (Eqs. (16), (19) and (20))
q^*, q_0^*	amount of solute in solid and saturation loading (Eqs. (13)–(15))
r	radial coordinate from centre of particle (Eq. (22))
r_0	particle radius (Eq. (21))
R	universal gas constant
t	time
T	absolute temperature
T_m	melting point of solute (Eq. (10))
S_a	cumulative mass of the analyte extracted (Eq. (24))
S_b	cumulative mass of the analyte extracted (Eq. (24))
S_t	mass of analyte removed by the extraction fluid after time t (Eq. (25))
S_0	initial total mass of analyte in the matrix in (Eqs. (24) and (25))
u	superficial velocity of the solvent (Eq. (16))
v_1^s, v_2^s	molar volume of supercritical fluid and solute (Eqs. (8), (10) and (11))
V	molar volume
V_a	volume extracted by S_a (Eq. (24))
V_b	volume extracted by S_b (Eq. (24))
y_i, y_j	mole fraction of component i,j (Eqs. (3) and (4))
y	mole fraction solubility (Eq. (6))
y_1, y_2	mole fraction of supercritical fluid and solvent (Eqs. (9)–(11))
z	axial position in the column

Greek letters

Φ_1	volume fraction of supercritical fluid (Eqs. (10) and (11))
δ_1, δ_2	solubility parameters for supercritical fluid and solute (Eqs. (8) and (10))
ϕ	axial dispersion coefficient (Eq. (21))
γ	porosity of particle (Eq. (22))
η, ν	parameters (Eq. (8))
θ	bed porosity (Eqs. (16) and (21))
ρ	density

presentations of various aspects on the use of this technology for extraction purpose are available in several critical reviews [1–20] and hundreds of other scientific articles. Some of these articles discuss the extraction of various organic compounds from plant matrices while others talk about the remediation of environment by supercritical fluid extraction (SFE) technique. Soil and groundwater contamination by inappropriate disposal of toxic, hazardous chemicals has been one of the major problems challenging the environmental concerns of both government and industry. In general, the options available for cleaning-up the soil contaminated by heavy, non-volatile organic compounds are limited, costly, and often inefficient [21]. Decontamination of soil is usually carried out by adding organic solvent into soil to extract the toxic compounds. However, the removal efficiency of this method is usually low and tends to create another problem to the environment as the solvent cannot entirely be removed from the soil matrices. Therefore, the extraction using supercritical fluid is considered a better way to remove the harmful aggregates from soil.

Reviews in the use of supercritical extraction technology for detachment of contaminant from soil and sediment have been given by several authors [2,14,17,18,20]. Comprehensive summary in experimental and theoretical studies on environmental supercritical extraction is also provided by Anitescu and Tavlaredis [2]. They abridged representative development in the field of polluted soil/sediment decontamination using supercritical extraction. Broad accomplishment of supercritical extraction through sustained research and its practice as a remedial technology were outlined. In their review they also compare the advantages and disadvantages of the relevant processes for remediation of contaminated soils/sediments. Bjorklund et al. [14] discussed the utility of selective supercritical extraction to study sorption/desorption process and bioavailability of persistent organic pollutants in sediments. Critical review by Dean [17] delineates the important practical considerations for the development of successful SFE of polycyclic aromatic hydrocarbons from environmental matrices. Bowadt and Hawthorne [18] address the attempts to understand the SFE process and its exercise to recover pollutants from environmental solids. They mention the fluid selection, temperature and pressure effects, collection analysis, and also comparison of the supercritical fluid technology with other conventional methods. Saldana et al. [20] focus their summary article on the removal of organic contaminants (such as petroleum hydrocarbons, polyaromatic hydrocarbons, polychlorinated biphenyls and others) as well as inorganic contaminants (such as heavy metals and radioactive elements) from soils. They conclude that more efforts are required to develop this technique into a commercial-scale economic remediation technology.

Even though many reviews are already available that deal with elimination of organic aggregates from different kinds of environmental samples, due to the complexity of many factors in effect within the process as well as the pronounced development of

Table 1
Comparison of physical properties of gases, SCF, and organic liquids

Phase	Density (g/cm^3)	Viscosity (P) $\times 10^4$	Diffusivity (cm^2/s) $\times 10^4$
Gases	~10^{-3}	0.4–3.4	100–10,000
Organic liquids	0.6–1.1	32–251	0.05–0.2
Supercritical fluid	0.2–0.9	2.1–10.8	0.11–3.45

the technique and increasing number of scientific publications in this area, their summary will not properly cover all the eminent aspects of the supercritical extraction process. We try to fill the gap by providing recent advances in supercritical extraction technology as applied into environmental decontamination purpose. This review focuses on the removal of hazardous substances, both organic and inorganic compounds, from distinctive types of solid matrices including animal and plant tissue and also liquids. New features on both experimental and modeling studies will also be considered in this paper.

2. Some important aspects in supercritical fluid extraction

2.1. Basics

Supercritical fluids are defined as fluids at certain temperature and pressure, which is above their critical value. Within the supercritical area only one state-of-the-fluid exists and it possesses both gas- and liquid-like properties. At this condition, gases will not be condensed by increasing the pressure. The phase diagram for gases at supercritical conditions is depicted in Fig. 1.

Supercritical fluids are unique solvents as their solvent effectiveness can be controlled by small changes in pressure as well as in temperature. Supercritical fluids have densities much greater than those of typical gases, slightly less than those of organic liquids. On the other hand, the viscosities of the supercritical fluids almost resemble those for typical gases, much less than those of liquids. These characteristic ensure high fluid phase capacity in concomitant with favorable transport properties, making supercritical fluids appealing to be applied as the solvent for extraction. Comparison of the density, viscosity and diffusivity of gases, supercritical fluids and organic liquids are summarized in Table 1 to give a clearer picture.

2.2. Trade-off aspects of supercritical fluid extraction

The superiorities of SFE over conventional extraction techniques lies upon: (1) its flexibility in terms of capability to adjust the solvent power/selectivity ratio of the supercritical fluids and (2) inherent nullification of organic solvent demand in process resulting in environment compliant techniques while also providing time and money cut-off required for solvent post-processing steps [1].
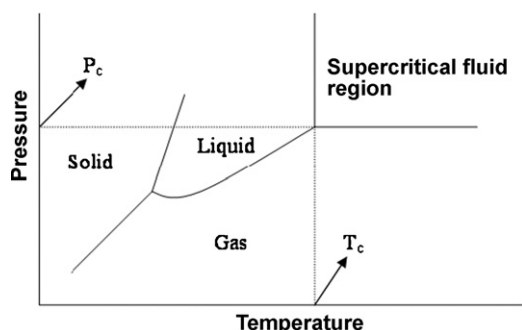

Fig. 1. Phase diagram for gases.

These aspects, however, is being traded-off by several factors such as: (1) higher investment cost as contrasted with that required by conventional technique [1,5] and (2) high pressure with its associated hazards, necessitates proper isolation equipment including its safety systems [5]. It should be emphasized here though that generally the operation scheme for SFE is quite cheap and once a certain SFE process module can be satisfactorily operated in laboratory scale, it will be easily scaled-up into commercial scale. Till today, SFE is utilized mainly in applications which is associated with high-value products or those required compliance with strict environmental regulations.

2.3. Technical aspects

Regularly, an SFE system incorporates a tank of the mobile phase, usually CO_2, a pump to pressurize the gas, an oven confining the extraction vessel, a restrictor to maintain a high pressure in the extraction line and trapping vessels. Analytes can be captured by letting the solute-containing supercritical fluid depressurize into an empty vial, through a solvent, or onto a solid sorbent material.

Extractions can be carried out in dynamic-, static-, or combination modes. An extraction in dynamic mode lets the supercritical fluid flows continuously through the sample in the extraction vessel and out the restrictor to the trapping vessel. In static-mode, the supercritical fluid circulates inside a loop containing the extraction vessel for some period of time before being released through the restrictor to the trapping vessel. In combination mode, a static-mode extraction is performed for some period of time followed by a dynamic-mode extraction afterwards.

Several gases or liquids are available to be employed as solvent in SFE such as ethylene, propane, carbon dioxide, ethane, benzene, etc. CO_2 in general is the most widely used and researched solvent because it is non-toxic, non-flammable, inert, readily available in high purity, cheap, has low surface tension and viscosity with high diffusivity [1,5,7]. Furthermore, CO_2 enables the supercritical condition to be attained at relatively low pressures and at near-room temperature as compared to other solvents also its high volatility makes it easy to be recovered in separators [1,5]. As addition, in the supercritical state, CO_2 has a polarity comparable to liquid pentane; therefore this gas at supercritical condition is suitable for lipophilic compounds. However, the major drawback of this gas lies on its lack of polarity, resulting in the bad performance for extraction of polar compounds [6,7].

The addition of co-solvents and surfactant to supercritical CO_2 can boost its extraction efficiency, especially for several hazardous organic compounds [22–35]. Incorporation of slight amounts of a hydrogen bond acceptor or Lewis base co-solvent compounds leads to high solubility amplification, as it reinforces solute–solvent interaction by means of: (1) incrementing density, (2) promoting certain chemical interactions, e.g. hydrogen bonding, (3) changing initial structure, e.g. swelling, or (4) rupturing solute–matrix interactions [5]. Table 2 sums up co-solvent/surfactant addition on the hazardous substances in supercritical fluid experiments. However, one major disadvantage of using co-solvent is the annihilation of the best characteristic of the SFE in which solvent-less operation is lost as another capital and energy intensive separation steps are required afterwards to separate co-solvent and hazardous compounds.

2.4. Performance-affecting factors

Pressure and temperature are prominent parameters on SFE, since both density and solvent capacity increase with pressure and decrease with temperature. The selection of operating parameters (pressure and temperature) depends on the specific compounds to

Table 2
Cosolvent/surfactant addition on the extraction of hazardous substances using supercritical extraction

Hazardous substances	Cosolvent/surfactant	Pressure (bar)	Temperature (K)	References
Anthracene, phenanthrene, pyrene, and perylene	Ethane, propane, butane, and methanol	100–350	313, 323, 333	[22]
2-Methyl-3-nitroanilin, 1,2 dinitrobenzene, 1,3 dinitrobenzene, 2,4,6 trinitrotoluene, and 2 nitrotoluene	Sodium dodecyl sulfate, sodium dodecyl ethersulfate, sodium diisooctyl sulfosuccinate, N-dodecyl pyridiniumchloride, nonylphenol ethoxylate, tridecyl ethoxylate, dodecyl ethpropoxylate, dodecyl polyglucose	150–500	323, 348, 373	[23]
Polycyclic aromatic hydrocarbon	Methanol	202, 252.5, 353.5	308, 323	[24]
Phenanthrene	Methanol	340, 408, 476, 544	343, 353, 373, 393	[25]
Chlorophenols	Methanol	328.3–555.5	363	[26]
Polychlorinated biphenyls	Dichloromethane	200	353	[27]
Organochlorine pesticides	Dichloromethane			[28]
1,1-bis(4-Chlorophenyl)-2,2-trichloroethane (DDT), polychlorinated-biphenyls (PCB)	Acetic acid, acetone, diethylamine, methanol, toluene	101	313	[29]
Polycyclic aromatic hydrocarbons	n-Pentane, acetone, toluene, dichloromethane, methanol	400	363	[30]
Polycyclic aromatic hydrocarbons	n-Hexane, cyclohexane, toluene, methyl-$tert$ butyl ether, methoxybenzene, dichloromethane, propane, pyridine, methanol	400	363	[31]
Polycyclic aromatic hydrocarbons	Methanol	400	363	[32]
Dioxins	Toluene	400	463	[33]
Polycyclic aromatic hydrocarbons	Methanol, diethylamine, toluene	404	353–473	[34]
Polycyclic aromatic hydrocarbons	Methanol, toluene, dichloromethane, ACN, acetone, and hexane	400	523 and 613	[35]

be extracted. Pressure is the most relevant process parameter to control the solvating power and extraction efficiency. Frequently the solvent power is described in the terms of supercritical fluid CO_2 density at the given operating conditions [1]. Fig. 2 shows the variation of CO_2 densities with pressure at various temperatures [36]. Apprehension of the relation between extraction performance and critical operating variables such as temperature, pressure, modifier type, solvent flow rate, etc., is indispensable for optimization and process design.

The efficacy of the supercritical extraction process also depends on the characteristic of the solid matrix such as particle size, shape, surface area and porosity. Specific interactions between solutes and active sites of the matrix could necessitate strict extraction conditions [6]. In outline, the extraction of hazardous materials from solid matrices (especially from porous materials) can be condensed into a four stage process: (1) diffusion of supercritical fluid into internal structure of porous material, (2) solubilization of solute into supercritical matrix, (3) diffusion of the mixture of solute and supercritical matrix to solid interface, and (4) diffusion of mixture to bulk supercritical fluid. Here, the physical characteristics of the solid such as pore size and connectivity are very crucial, since the supercritical fluid should be able to disperse within the solid matrix during the supercritical extraction process. Particle size also plays an important role in the supercritical extraction process. Decreasing particle size of the solid matrices (especially for porous materials such as soil, clay, and activated carbon) causing the rise in extraction efficiency, due to the shorter diffusion pathway. In dynamic-mode SFE operation, another vital parameter is CO_2 flow rate. Lower CO_2 flow rate as proportional to slower fluid velocity end up with more chance to diffuse into solid interior, leading to advanced extraction yield.

In principle, the extraction rate relies upon two controlling factors: (1) thermodynamics, as represented by solubility or elution step and (2) kinetics, corresponds to desorption step [2]. The slowest step determines overall process rate. CO_2 flow rate can be adjusted to boost the extraction rate if the controlling step is the solubility process [1,2]. If the kinetics play significant role in extraction, then the particle size can be reduced to improve the rate. Dynamic mode is most suitable for operation limited by thermodynamics factors while either static/dynamic mode can be used equally effective for kinetically determined extraction process [2].

3. Solubility studies of hazardous substances under SCF condition

Several variables can play role in SFE and the choice of extraction conditions has been largely determined empirically. One preliminary area that must be assessed is the solubility of the compound to be extracted in the supercritical fluid. Solute solubility in supercritical fluid depends on many factors such as solute and supercritical fluid structure, thermodynamic property, specific solute–supercritical fluid interactions, etc. The solubility of solids and liquids in supercritical fluids needs careful consideration in the development of any supercritical extraction process. In the litera-
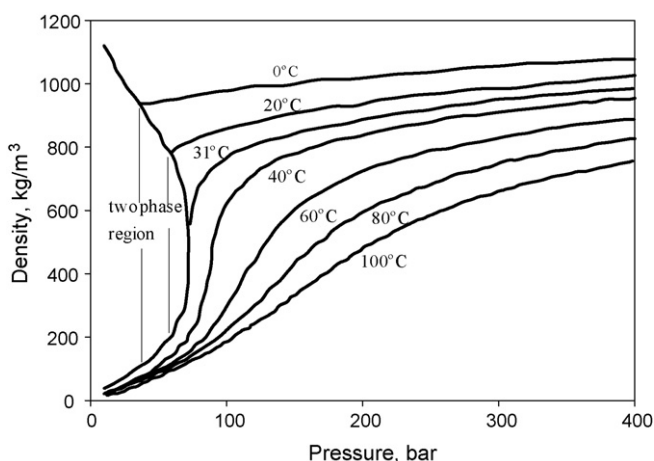

Fig. 2. Density behavior of CO_2 calculated by equation of Bender. Adapted from ref. [36].

Table 3
Solubility studies of hazardous compounds under supercritical CO_2 conditions

Hazardous compounds	Pressure (bar)	Temperatures (K)	References
Naphthalene	0–207.7	372.45, 403.85, and 430.65	[37]
Acenaphthene, fluoranthene, and triphenylene	121.6–354.6	308–348	[38]
9-Nitroanthracene and 2-methylanthracene	122–355	318–348	[39]
Azobenzene, *p*-hydroxyazobenzene, and *p*-dimethylaminoazobenzene	91–253	308.2 and 318.2	[40]
Naphthalene and pentachlorophenol	83.2–254	294, 299.3, 307.8	[41]
Pyrene, chrysene, perylene, and benzo[*ghi*]perylene	100–450	313–523	[42]
Ethyl phenyl sulfide (EPS) and 2-chloroethyl ethyl sulfide (CEES)	23.7–237	298–373	[43]
Anthracene, phenanthrene, pyrene, and perylene	100–350	313, 323, 333	[22,44]
l,l-bis(4-Chlorophenyl)-2,2,2-trichloroethane (DDT) and (2,4-dichlorophenoxy)acetic acid (2,4-D)	104–208	313, 323, 333	[45]
Hexachlorobenzene and pentachlorophenol	90–236.5	308, 318, 328	[46]
Acenaphthene, fluoranthene, and triphenylene	121.6–354.6	308–338	[47]
Polychlorinated biphenyl (PCB) congeners	100–300	313, 323, 333	[48]
Ametryne, prometryne, atrazine and simazine	100–300	313, 333, 353	[49]
Naphthalene and phenanthrene	48–280	308.2	[50]
4,4′-Dichlorobiphenyl, 2,3′,4′,5-tetrachlorobiphenyl, and 2,2′,3,3′,4,4′-hexachlorobiphenyl	90.9–485	308.1–323.1	[51]
Methoxychlor, endrin, and lindane	100 and 220	313.1 and 331.1	[52]

ture, solubility measurements for numerous hazardous solutes in a number of supercritical fluids have been reported [37–52]. The list of solubility studies for several hazardous compounds is condensed in Table 3. Several correlations have been developed in order to correlate and extrapolate solubility data at various pressures and temperatures. Some of these correlations are highly empirical, while some have strong fundamental basis. However, in most cases, these correlations still need one or more adjustable fitting parameters, necessitates the experimental data existence. In this review, we will limit our focus into the solubility of hazardous compounds in supercritical carbon dioxide.

Solubility data of single hazardous component in supercritical fluids have been tabulated in the literature for a number of different components [37–52]. Due to strong dependence of solubility on density, temperature and pressure of supercritical fluids, extensive amount of data are still needed. However, reliable experimental solubilities data are difficult and time consuming as well as expensive to obtain, it is desirable to have a tool for predicting the solubility data in supercritical fluids over a wide range of pressure and temperature based on the available data in the literature. For this purpose, several models have been developed and tested, and these models mainly use either: (1) an equation of state (EOS) approach, (2) semi empirical approach, (3) a density-based approach, or (4) a solubility parameter approach [53,54].

In the equation of state approach, the supercritical fluid is assumed as high-pressure gas while in other approaches the supercritical fluid is treated as a liquid. A number of equations of state (EOS) models are available of which the most commonly used are Peng–Robinson [43,45,46,50,51], and modified form of Redlich–Kwong equation of state as derived by Soave (SRK) [37,51]. Peng–Robinson equation has the following form.

$$P = \frac{RT}{(V - b)} - \frac{a(T)}{V^2 + 2bV - b^2} \quad (1)$$

and Soave–Redlich–Kwong equation of state has the form

$$P = \frac{RT}{V - b} - \frac{a(T)}{V(V + b)} \quad (2)$$

The constant *a*, which is a function of temperature altogether with *b*, can be calculated using several mixing rules such as Huron–Vidal [37], van der Waals [43,45], or Wong–Sandler [46].

Recently, Harris et al. [37] investigated high pressure vapor–liquid equilibrium of naphthalene and benzoic acid with supercritical CO_2. Using the experimental data obtained, they successfully predicted the solubility data and exploit the data to derive the optimized gas–solvent group interaction parameters

for the predictive Soave–Redlich–Kwong equation of state. Solubility of 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane (DDT) and (2,4-dichlorophenoxy)acetic acid (2,4-D) in supercritical carbon dioxide and supercritical carbon dioxide saturated with water was reported by Macnaughton and Foster [45]. Their experimental data were correlated using the original and modified form of the Peng–Robinson equation of state. Even though modeling result reflected the fact that the presence of water in supercritical CO_2 had no significant influence on the solubility of DDT, the solubility of 2,4-D surprisingly arises in the presence of water.

The importance of mixture solubilities cannot be underestimated especially when supercritical processes involving separation of multicomponent mixtures and extraction of mixtures from solid matrices such as regeneration of spent adsorbents or remediation of contaminated soil are associated. Hexachlorobenzene and pentachlorophenol are carcinogen chemicals. Peng–Robinson equation of state with Wong–Sandler mixing rules was utilized by Cross and Akgerman [46] to predict the solubility of carcinogenic mixture of hexachlorobenzene and pentachlorophenol under supercritical CO_2 condition. They also scrutinized Wong–Sandler mixture combination rules to delineate the supercritical system in order to eliminate the need for temperature-dependent binary interaction parameters. Despite the fact that the model they used is quite simple, i.e. only requires excess Helmholtz energy at infinite pressure and an infinite pressure activity coefficient, it is capable to well-match the solubility data of hexachlorobenzene and pentachlorophenol.

Liu and Nagahama [50] resort to a continuous gas flow apparatus to determine the solubilities of naphthalene and phenanthrene in $SCCO_2$, phenanthrene in SC-fluoroform (CHF_3), and also naphthalene and phenanthrene in SC-fluoroform at 308.2 K and 4.8–28 MPa. These authors contrasted the suitability of three different equations of state (Peng–Robinson, Soave–Redlich–Kwong, and Yu–Lu–Iwai) and some simple density-dependent correlations to fit the solubility data. Among the three EOSs, the YLI-EOS with two binary parameters is deemed to provide the best representation of the experimental solubilities as a whole. For the sake of acquiring better representation of solid solubilities in supercritical fluids, Liu and Nagahama also employed two simple density-dependent equations for the prediction of their experimental data. They concluded that these simple equations also match the solubilities data properly, especially in high-density region ($0.5 < \rho < 1.1$).

Solubilities of polychlorinated biphenyls (PCBs), e.g. compounds with 1–10 Cl atoms attached to biphenyl on supercritical carbon dioxide were also studied by Yu et al. [51] at temperature of 308.1–323.1 K and at a pressure range between 90 and 480 atm.

They correlated the experimental data using Peng–Robinson equation of state and a volume based linear model as developed by Wang and Tavlarides [55]. The unknown critical properties of the polychlorinated biphenyl congeners were estimated using group contribution methods, and the vapor pressure data were determined by the modified Watson method. The solubilities of PCB's congeners (related chemicals, i.e. its derivatives) tend to become diminished with the number of chlorines on the benzene rings.

The use of chelating agents in coupled with supercritical solvents instead of conventional organic liquid solvents for the extraction of metals and radionuclides has become an advancing field of interest around chemical engineering and chemistry research community. Chelation, when used in conjunction with non-toxic and abundant solvents such as supercritical carbon dioxide, may indeed provide more environmentally sound and cost-effective technologies to replace some obsolete chemical and metallurgical separations and manufacturing processes still in use until today [56]. Peng–Robinson equation of state was chosen by Cross et al. [56] for the thermodynamics modeling of chelate complex solubility in supercritical carbon dioxide. The model incorporated van der Waals-1 mixing rules as shown below.

$$a = \sum_i \sum_j y_i y_j a_{ij} \tag{3}$$

$$b = \sum_i \sum_j y_i y_j b_{ij} \tag{4}$$

They used cupric acetylacetonate and diethyldithiocarbonate as the chelate complex models. These equations are claimed to correlate the chelate complex solubility data relatively well in their studies.

Escobedo-Alvarado et al. [57] examined the applicability of several cubic equation of state-G^x model to predict the solid-supercritical fluid phase equilibria. van der Waals, WS-UNIQUAC and WS-NRTL are employed here as the equation of state-G^x models. In order to test the models, they took already-available solubility data from literature such as naphthalene, 2,3-dimethylnaphtalene, 2,6-dimethylnaphthalene, benzoic acid, anthracene, phenanthrene, and 1,10-decanediol. They came at conclusion that the equation of state-G^x model is capable to give a good correlation of the solubility of single component in a supercritical fluid.

Another alternative equation of state that was also tested to fit the solubility in supercritical fluid is Patel–Teja equation of state. Sheng et al. [58] obtained the solubility of five aromatic compounds in supercritical carbon dioxide and fit those data into Patel–Teja equation of state with UNIFAC group contribution liquid model as the excess free energy model.

One more distinct approach to correlate the solubility data in supercritical fluids relies upon density-based correlation. The development of this approach based on the collective observation that the logarithm of the solubility is linearly dependent on the density [53]. This method is also widely used to correlate the experimental solubility data. Chrastil [59] was the pioneer in establishing a semi-empirical solubility equation based on this approach. He assumed that the molecules of the solute associate with the molecules of the gas are in equilibrium with solvato complex: $A + kB \leftrightarrow AB_k$, so that the equilibrium concentration can be calculated from the law mass action. The semi-empirical Chrastil equation has the form of:

$$c = d^k \exp\left(\frac{a'}{T + b'}\right) \tag{5}$$

They exposed that in most cases, the solvato complex was not stoichiometric, so that the association constant k expresses an average equilibrium association number, which is a characteristic constant for a given gas and solute. Knez et al. [49] used two different equations to correlate the solubility of solid s-triazine derivatives, i.e. ametryne, prometryne, atrazine and simazine in supercritical CO_2, of which one among them is Chrastil equation. Chrastil's model suggests that plots of $\log c$ against $\log d$ would yield straight parallel lines for different temperatures. In the case of solubilities for s-triazine derivatives, Knez et al. stated that the thermodynamic formalism of $\log c$ against $\log r$ established to correlate solute CO_2 solubilities in SCF as a function of density was deemed more suitable for non-polar solutes.

Beside Chrastil equation, another consecutive semi empirical density-based correlation, proposed by Bartle et al. [60], has the form.

$$\ln\left(\frac{yP}{P_{\text{ref}}}\right) = A + C(\rho - \rho_{\text{ref}}) \tag{6}$$

The value of A is predicted by

$$A = \frac{h + g}{T} \tag{7}$$

The value of C in Eq. (6), results physically from solvation of the solute by the supercritical fluid, is assumed to remain constant. This semi-empirical equation has been applied to predict the solubility of hazardous compounds in supercritical fluid by Yamini and Bahramifar [38], Yamini et al. [39], and Miller et al. [42].

Solubility parameters can also be used to equate solubility of hazardous substances in supercritical fluids [40]. For the representation of solubility utilizing this approach, the as-established models are grounded upon Scatchard–Hildebrand regular solution theory. Ziger and Eckert [61] introduced an equation with the solubility parameter approach combined with the van der Waal equation of state to describe the solubility data.

$$\ln E = \eta \left[\frac{v_2^s(2\delta_1\delta_2 - \delta_1^2)}{RT} - \ln\left(1 + \frac{\delta_1^2}{P}\right) \right] + v \tag{8}$$

E is defined by

$$E = \frac{y_2 P}{P_2^{\text{sat}}} \tag{9}$$

Another density-dependent solute solubility parameter to correlate solubility in supercritical fluids was unraveled by Guigard and Stiver [53] as follows.

$$y_2 = \exp\left[\frac{-\Delta H_{\text{fus}}^m}{RT_m}\left(\frac{T_m}{T} - 1\right) - \frac{v_2^s \Phi_1^2}{RT}(\delta_2 - \delta_1)^2 \right] \tag{10}$$

Φ_1 is detailed by:

$$\Phi_1 = \frac{y_1 v_1^s}{y_1 v_1^s + y_2 v_2^s} \tag{11}$$

In pursuance of representing the phase equilibria for solid-supercritical fluid systems, a different model has been established by Zhong et al. [62]. The model originated from the fact that the free solute and solvent molecules and solute–solvent clusters in such a solid-supercritical fluid system are in chemical equilibrium. In here, several other assumptions were also added to construct the model. The model as acquired by Zhong et al. comprises several parameters, and they utilized the local density of the solvent surrounding a solute as one of the parameter. Solubilities of several hazardous compounds such as naphthalene, phenanthrene, pyrene, etc., have been fitted using this equation.

Many other different types of models based on thermodynamic, molecular simulation, and solution approach have been presented by several researchers in the interest of correlating the solubilities of hazardous substances in supercritical conditions, for example,

Lennard–Jones chain (PLJC) equation of state [63], solution model approach [64], simplified cluster solvation model [65], SAFT equation of state [66], Monte Carlo simulation [67–70], wavelet neural network [71] and theory of dilute solution [72].

4. Hazardous substances extraction from soil and sediment

Owing to their high chemical and biological stability accompanied with strong lipophilicity, persistent organic pollutants, like polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), chlorobenzenes and pesticides, create serious environmental problems. These pollutants leach into soil, sediment, and groundwater and finally, adulterate the food chain. The desire to lessen the use of hazardous organic solvents in analytical extraction in the last few years has promoted the breakthrough in novel technologies that require less solvent as contrastive to classical extraction necessity. Supercritical CO_2 especially, has become a more viable option in distinctive industrial and environmental cleaning processes. As a complement to its environmentally benign nature, its adaptable thermodynamic properties accompanied by higher diffusion property further strengthen this fluid as a favorable solvent. A number of experiments have been carried out to eliminate toxic or industrial waste compounds from soil by SFE.

Polycyclic aromatic hydrocarbons are widespread organic compounds in the form of fused aromatic rings available in a wide range of molecular weights and boiling points that tend to be prevalent in soil. These pollutants mainly formed by incomplete combustion of carbon-containing fuels and frequently introduced into soil either by industrial discharges or petroleum spills. Once entering the soil matrices, due to their low solubility and vapor pressure which is even lowered for higher molecular weight compounds, PAHs would then be adsorbed on soil and deposited in the matrices. Several studies on the detachment of these compounds from soil exploiting SFE technology have been conducted by numerous researchers [22,30–32,34,35,73–97].

PAHs commonly present in ubiquitous amount within soils. They tend to bind to organic compounds in soils. As a result, the supercritical extraction of PAHs from soils with a high concentration of humic substances is difficult [30]. The incorporation of small concentration of organic solvents to the supercritical fluids (usually carbon dioxide) leads to an increase in extraction efficiency. Lutermann et al. and Hollender et al. [30–32] studied the effects of co-solvent addition on the elimination of PAHs from two real environmental soil samples using SFE. In general, they claimed that the efficiency of PAHs (especially high molecular weight PAHs) removal escalate with diminished polarity and stronger concentration of the co-solvent used. They also opposed the result with the supercritical extraction using pure CO_2. The use of co-solvent significantly increased the recovery of PAHs from soil with high content of humic acids. The co-solvents used have different physical and chemical properties which can break the hazardous compounds–soil matrix interactions such as van der Waals forces, electron donor–electron acceptor interactions and hydrogen bonding. The dipole moment, Bronsted acidity or basicity of these co-solvents also play substantial role in disrupting hazardous compounds–soil matrix interactions [31]. Lojkova et al. [35] resorted to two-step procedure for the SFE of PAHs from soil samples. Their procedure includes a static supercritical fluid treatment as the first step followed by SFE with solvent trapping as the second step. The SFE yields 220–300% of naphthalene, 180–240% of acenaphtylene, and 120–150% of acenaphthene of that achieved using Soxhlet extraction.

Barnabas et al. [73] have analyzed the extraction of 16 polycyclic aromatic hydrocarbons using supercritical CO_2. An experimental design approach, based on a central composite design, was exploited to determine which supercritical extraction operating variables affect the total recovery of polycyclic aromatic hydrocarbons. In the study, Barnabas et al. [73] chose pressure, temperature, extraction time, and percent of modifier added as the operating parameters. A statistical treatment of the results indicated that extraction lime and percent modifier addition were the *only* variables to significantly affect PAH recovery. A comparison between different extraction techniques such as microwave assisted extraction, SFE, subcritical solvent extraction, sonication and soxhlet extraction for the removal of PAHs was carried out by Dupeyron et al. [74]. Conventional procedures (Soxhlet and sonication), presented quantitative results which were less satisfactory than microwave assisted extraction, SFE and subcritical solvent extraction since they demonstrate a greater dispersion. Another comparison between soxhlet, microwave-assisted extraction and supercritical extraction was made by Dean et al. [97]. They employed each technique to extract 16 PAHs from a native contaminated soil. The removal efficiency in their findings goes in the order of supercritical fluid extraction > microwave extraction > soxhlet extraction. Becnel and Dooley [91] have also studied the supercritical extraction of polycyclic aromatic hydrocarbon mixtures from contaminated soils. Effects of supercritical density, temperature, co-solvent type and of slurrying the soil with water were examined. They found that the temperature had significant effect on the total recoveries and initial rates, while other variables only gave slight influence.

Study of remediation of flare pit soils using SFE was carried out by Nagpal and Guigard [75]. The extraction experiments were performed on two flare pit soils from two sites in Alberta at pressures ranging from 11.0 to 24.1 MPa and temperatures between 40 and 80 °C. The observed effects of pressure, temperature, density, soil type and supercritical CO_2 flow rate on the recovery of PAHs were collected. Analyzing the results they ascertained that the extraction efficiency was both pressure and temperature dependent as expected. The soil particle size also affected extraction efficiency, with coarse-grained sand exerted higher extraction efficiency than fine-texture loam, this phenomena occurred due to the different characteristic of soils studied.

PAHs also exist as predominant pollutants in marine sediments. These organics enter waters and marine sediments through storm runoff, industrial discharges, and petroleum spills. Once assimilated into the marine environment, PAHs either stays in the water column or, adsorbed onto particulates, and become deposited in bottom sediments. Several studies of supercritical extraction of PAHs from marine sediments have been conducted in the last few years [76,78,81]. Because of numerous advantages in extraction time, solvent, fluid quantities, and costs, combination of the extraction techniques using accelerated solvent and SFE was evaluated in order to achieve quantitative yields of PAHs from marine sediments [81]. Combination of accelerated solvent and SFE enhanced the extraction efficiency recovery for 5- and 6-ring PAHs.

Wright et al. [93] performed the supercritical extraction of soil samples containing coal tar residues from manufactured gas plants. In their study, they also compared the effectiveness of supercritical extraction with soxhlet extraction techniques. They claimed that for supercritical extraction, removal efficiencies of greater than 80–100% could be achieved in the first 30 min. However, the performance of supercritical fluid to remove high molecular weight polycyclic aromatic hydrocarbons is poor due to their lower solubilities in supercritical CO_2. Another study of coal tar detachment from contaminated soil was conducted by Yu et al. [94], and 92% removal of the polycyclic aromatic hydrocarbon was obtained in 7 h extraction period. Andrews et al. [95] considered the adsorptive behavior of several PAHs (phenanthrene, anthracene, triphenylene
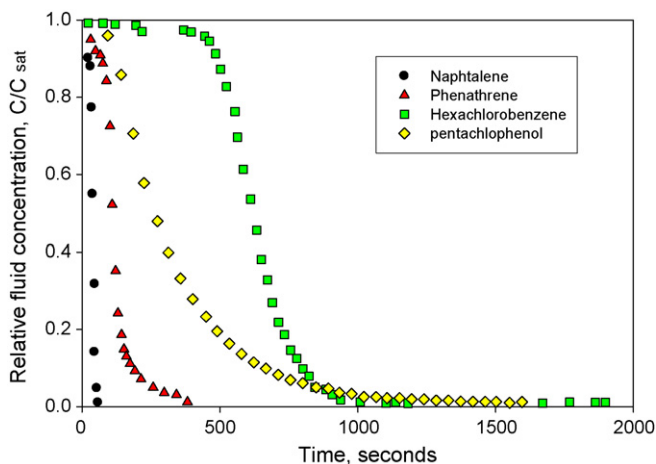
Fig. 3. Desorption profiles of the organics from soil at 308 K. Naphthalene and phenanthrene extraction at 100 atm pressure and hexachlorobenzene and pentachlorophenol at 113 atm. Adapted from ref. [109].

and perylene) from supercritical CO_2 onto sandy loam-type soil. They found that soil adsorption isotherms for these compounds could be correlated by means of Freundlich and BET adsorption models.

Supercritical CO_2 was used by Champagne and Bienkowski [96] to extract anthracene and pyrene from a model soil at conditions ranging from 35 to 55 °C and 77.9–241.3 bar. They confirmed that the isotherms on model soil for both of polycyclic aromatic hydrocarbons followed the Freundlich isotherm. They also examined the effect of additional water in the soil phase on equilibrium.

Supercritical extraction of PCBs from soil matrices has been investigated by many researchers for several years. Dooley et al. [98] perform the supercritical extraction of PCBs from highly contaminated top soils at 313 K and 101 bar. A supercritical extraction was applied to a soil artificially contaminated with PCBs [99]. Another supercritical extraction of PCBs from soil were carried out by Chen et al. [100], Bjorklund et al. [101], Pilorz et al. [102], Yak et al. [103], Pross et al. [104], Westbom et al. [105], Hawthorne et al. [106] and Nilsson et al. [107].

Supercritical fluid has been proved as a valuable tool in environmental remediation that requires separations. Separation of several other toxic organic compounds, herbicides, pesticides and insecticides from soil using supercritical CO_2 have been well-attained by different research groups. Lopezavilla et al. [108] carried out the supercritical extraction of chlorophenoxy acid herbicides from solid sample at 400 atm and 80 °C. They also tested the effect upon addition of derivatization agent such as tetrabutylammonium hydroxide, methyl iodide as well as others derivatization agents.

A supercritical extraction process applied into remediation of soils contaminated with heavy molecular weight organic compounds has been proposed by Madras et al. [109,110]. In the suggested process, the organic compounds were continuously extracted from soil using supercritical CO_2 and then the extracted mixture is exposed onto activated carbon. The organic compounds tested in their experiments were naphthalene, phenanthrene, hexachlorobenzene, and pentachlorophenol. The supercritical desorption profiles of the organic compounds studied are shown in Fig. 3. From this figure, it is deemed that the organic compounds can be completely removed from soil in a short time.

Another supercritical experiment for removal of herbicides from soil was conducted by Locke [111]. As the herbicide model, 14 C-ring-labeled fluometuron (*n,n*-dimethyl-*n'*-[3-(trifluoromethyl)phenyl]urea) was chosen. The optimum condition for removal of 14 C-ring-labeled fluorometuron was attained at 50 °C with CO_2 density of 0.8 g/cm^3 using static extraction times greater than 6 min as opposed to dynamic extraction times of greater than 18 min. Removal of two sulfonylurea herbicides in four soils sample was performed by Berdeaux at al. [112]. As solvent, they used supercritical CO_2 with methanol and water as modifiers. From their experimental results, they concluded that the recovery rates were good (>80%) for all types of the studied soils except for those with high organic carbon content. Another supercritical study using sulfonylurea herbicides as model compounds was conducted by Berglof et al. [113]. Yarita et al. [114] investigated a method for removal of triazine herbicides from soil using supercritical carbon dioxide as the solvent. They found that the recoveries of triazine herbicides increased with the increase in both extraction pressure and temperature. They also checked the effect of concentration of triazin and methanol added as modifier on removal effectiveness. Another study of the removal of triazine using supercritical carbon dioxide was also carried out by Papilloud and Haerdi [115].

Herbicides migration from soils to ground water or surface water relies upon the characteristic of soil matrix. Desorption model is a common tool used to predict the release of this contaminant into water. Therefore, it is considered important to obtain accurate measurement of the sorption equilibria for herbicides in soils. Rochette and Koskinen [116] used supercritical carbon dioxide in determining sorption coefficients of antrazine in field-moist soils. They found that soil/water partition coefficients at a supercritical CO_2 density of 0.25 g/l were linearly related to soil organic carbon content, clay content, and Freundlich parameter.

S-2,3,3-Trichloroallyl diisopropylthiocarbamate (triallate) is a herbicide made for weed control in cereal, legume and beet crop. Elimination of this substance from soils by organic solvent extraction method is regarded as difficult and expensive operation as triallate is firmly adsorbed by soils. The use of supercritical fluid technology for remediation of soils contaminated by triallate was initialized by Bernal et al. [117]. Triallate was extracted at a density of 0.65 g/ml at a CO_2 flow rate of 1 ml/min with extraction time of 25 min. However, the removal efficiency of this herbicide from aged soil using pure supercritical carbon dioxide was lower than solvent extraction due to its lack of polarity for the extraction of polar compounds.

Pesticides contamination on soils is yet another major problem for the environment. One of the best methods available among many methods proposed to remove this pollutant from soil is supercritical extraction. Different supercritical experiments to detach pesticides from soil have been conducted using different types of pesticides. Reimer et al. [28] has developed a method for extraction of 21 organochlorine pesticides from soil using carbon dioxide as the supercritical solvent. In their extraction experiments, they used dichloromethane as co-solvent and magnesium sulfate as drying agent. Removal efficiency from six different soils in their experiments ranged from 70% to 95%. SFE of carbamate pesticides (propoxur, aminocarb, carbanyl, and methiocarb) from soils and cereals at 378 bar and 54 °C has been carried out by Izquierdo et al. [118]. They advised that the recoveries of these pesticides depend on analyte and soil components. The influence of matrix properties on SFE of organochlorine pesticides from sulfur-containing soils was inferred by Ling and Liao [119]. They also examine the role of total organic carbon, pH, moisture content, and grain size toward removal efficiency of 16 organochlorine pesticides. It is confirmed that the extractability of pesticide residues from soil samples is strongly affected by environmental variables and SFE parameters. To further verify the most significant variables, a multivariate optimization scheme (MOS) was employed by Zhou et al. [120] to investigate the effects of those parameters on the extractability

of several pesticides from soil. Later, they concluded that the extractability of pesticides residues from soil was also dependent on the particular pesticide examined and on the nature of residues. Other reports dealing with pesticides removal from soils using SFE were performed by Koinecke et al. [121] and Sahle-Demessie and Richardson [122]. Koinecke et al. conducted their experiments in the temperatures range of 60–70 °C and at a pressure of 380 bar. Fenpropimorph, pirimicarb, parathion-ethyl, triallate and fenvalerate are utilized as pesticide residues. The best removal efficiency can be attained at 60 °C with 5% methanol as modifier. These authors also tried the supercritical extraction of high contaminate soil on a bench-scale supercritical extraction unit. They assessed the performance of supercritical extraction using pure and modified carbon dioxide as the solvent. They claimed that the best operating condition was achieved at 30 min extraction time, 80 °C, and at pressure of 300 bar with the removal efficiency more than 98%.

A tendency toward more time-effective and environment-friendly processes has boosted the interest in SFE. Few approaches have dealt with multi residue analysis of pesticides in soils, which present an additional complexity due to the disparity of chemical structures, solubilities in the extraction fluid and interaction with the matrix. A number of experiments using SFE for analysis of herbicides and pesticides in soils samples are available in the literatures [123–126]. In general, the use of supercritical fluid technology for the analysis of hazardous materials within soils creates many advantages such as rapidity, simplicity, great analyte selectivity, good extraction efficiency, clean-up step elimination, suitability for thermally labile compounds, automation, solventless or near solvent free character and reduced environmental hazard.

Polycyclic aromatic nitrogen heterocycles (PANHs), the N-heterocyclic analogue of PAHs belong to the class of the biologically active environmental pollutants with both mutagenic and carcinogenic properties. Extraction recovery of 10 selected polycyclic aromatic nitrogen heterocycles (PANHs), quinoline, 2-methylquinoline, 6-methylquinoline, 8-methylquinoline, acridine, benzo[h]quinoline, phenanthridine, indole, 2-methylindole, and carbazole from spiked (injected with pollutant compounds) soil samples was carried out by Koci et al. [127]. They contrasted the performance of four dissimilar extraction methods (pressurized solvent extraction, SFE, soxhlet warm extraction, and standard soxhlet extraction) to recover these hazardous compounds from spiked soil samples. As expected, the SFE showed the higher recovery result.

Contamination of soil by petroleum hydrocarbons poses a major environmental problem. The sources of petroleum hydrocarbon contaminant in soil include crude oil leaks from pipelines, spills around production areas, disposal of refinery wastes, and transport fuels leaking from underground storage tanks, etc. The recovery of petroleum hydrocarbon from soil remains a challenge due to the difficulties encountered during the process, since the binding of petroleum hydrocarbons with a soil might occur through a number of mechanisms which are influenced largely by the textural property of the soil as well as its organic and moisture content. Conventional methods to detach this pollutant from soils are time consuming and end up in another solvent waste problem, so super-critical fluid has been shown to be preferred alternative method for the removal this contaminant from soils [128,129].

Composting of garden wastes as an alternative to land-filling is not economically feasible unless the cost of processing compost can be offseted by revenues gained from selling the resultant composts. Garden waste, including grass clippings from lawns treated with pesticides, generally contains pesticide residues. Bakiomah et al. [130] adopted a new method for simultaneous supercritical carbon dioxide extraction of chlorpyrifos and its primary degradate, 3,5,6-trichloro-2-pyridinol (TCP), from garden compost. They suggested that in situ derivatization with N,O-bis(trimethylsilyl) trifluoracetamide was required for extraction of TCP.

It must be mentioned here that in many studies as reported above, variation exist in terms of the samples. Samples can be either a spiked (injected) or real-world sample. The latter sample commonly has been subjected to numerous processes such as aging, weathering, chemisorption, etc. that cause them to bind the pollutants tighter.

5. Herbicides and pesticides extraction from plant matrices

The requirement to analyze and ascertain foreign substances in fruits and vegetables in which their presence being due to chemical and technological treatments or processes or through environmental pollution has become a substantial issue nowadays. The determination of pesticide and herbicide residues content on fruit and vegetable products has thus become a more and more strict requirement for consumers, producers and the authorities that are responsible for quality controls. In general, the presence of organic contaminants in fruit and vegetable samples cannot be analyzed without some preliminary preparation due to the complexity of solid matrices and very low concentration of organic contaminants. As a consequence, the need has arisen to set up increasingly fast and simple analysis methods which can provide the largest possible range of results. The drawbacks associated with classical extraction techniques such as the need for large amounts of solvents, time-consuming and considerable waste products treatment, have been overcome by the commencement of matrix solid-phase dispersion in combination with SFE. To date, SFE has also been regarded as an efficient and rapid method for the isolation of hazardous compounds from various kinds of plant matrices. Studies on the removal or analysis of hazardous compounds (pesticides and herbicides) from various kinds of plants matrices have been conducted by many authors [131–144] and a brief description of their studies is outlined in Table 4.

Following the exposure of supercritical fluids to fruits or vegetables samples, the extract mixtures containing the hazardous substances can be directly analyzed using GC without the necessity for any further purification process. Moreover, this technique gives surpassing efficiency than those conventional ones. Satisfactory extraction efficiencies were reported for non-polar to low polar pesticides such as organochlorine [131,133,135,137,139,141–144] and organophosphorus [131,136,137,141,143]. For pesticides of high polarity including its metabolites, the addition of polar modifiers such as methanol [132,136,138,139], acetone [133,134,136,138], hexane [133,138], ethanol absolute [133], water [132] or water + ethanol mixture [133] to CO_2 enhances its dissolving power. Nevertheless, the type of polar modifiers added requires careful consideration, since the matrix-swelling effect also plays a vital role in extraction efficiency [133].

Earlier, it has been suggested that vegetation can act as an indicator of atmospheric contamination, a sink of pollutants as well as a tool to study the uptake mechanism of atmospheric organic. The mechanism of vegetation uptake of organic pollutants is governed by the chemical and physical properties of the pollutant, environmental conditions, and the plant species [145]. Among miscellaneous atmospheric organic pollutants, PAHs are the most intensively studied compounds. The extraction of PAHs from plant matrices using SFE was executed by Lang et al. [146]. Fresh and fallen pine needles are picked as the plant matrices. SFE using toluene-modified CO_2 is stated as an effective, more selective and faster extraction technique for contaminant analysis from vegetation matrices in this study.

Table 4
Removal of hazardous compounds from plant matrices

Plant	Hazardous substances extracted	Operating conditions	Recovery	References
Apple	Chlorinated, organophosphorous, organonitrogenous, and pyrethroid pesticides	Temperature: 318 K; CO_2 density: 0.6 and 0.8 g/l; extraction time: 10 min; liquid CO_2 flow rate: 2.5 ml/min; pressure 189 bar	Chlorinated pesticides: 52–76%, organophosphorous and organonitrogenous pesticides: 69–128%, pyrethroid pesticides: 84–91%	[131]
Melon	Insecticides fipronil, acrinathrin and pyridaben and the fungicide kresoxim-methyl	Temperature: 50 °C; pressure 303 bar; CO_2 flow rate: 1.0–1.2 ml/min; methanol and water were used as modifier	Fipronil: 89–101%, kresoxim-methyl: 83–86%, acrinatrin: 72–78%, pyridaben: 98–104%	[132]
Ginseng	α, β, γ and δ-Benzene hexachloride (BHC), penthchloronitrobenzene and DDT and its metabolites	Temperature, 40, 50 and 60 °C; pressure: 150–350 bar; modifier used: absolute ethanol, acetone, and normal hexane, ethanol + water	80–190% depends on the modifier used and trap materials	[133]
Fresh fruits (apple and banana), Vegetables (Radish, cucumber, and potato) and rice	18 pesticides (inabenfide, myclobutanil, imazalil, triflumizol, etc.)	Temperature 40 °C; pressure: 300 bar; CO_2 flow rate: 4.9 ml/min; modifier used: acetone; extraction time: 40 min	>50% depends on the plant matrices and pesticides used	[134]
Radix Codonopsis	12 organochlorine pesticides	Pure CO_2, extraction pressure 150 bar; extraction temperature 60 °C; extraction time 20 min and flow rate 55 ml/h	Higher than 93.5%	[135]
Lettuce, apple, potato, and tomato	Four pesticide classes (organochlorine, organonitrogen, organophosphorus and pyretroid)	Temperature: 70 °C; pressure: 199.71, 449.35 and 698.98 bar, using a flow rate of expanded gas of 1.5 ml min^{-1} for 25 min, methanol and acetone were used as modifier	74–96%	[136]
Spinach, soybean and orange	303 pesticides compounds	CO_2 density of 0.819 g/ml (172 bar, 40 °C); 15 min static time, 15 min dynamic extraction time. The dynamic flow of supercritical CO_2 was 2–3 ml/min for a 10 ml sample cartridge. Acetone was used as a collection solvent	70–120% recovery for more than 80% of the examined compounds	[137]
Sugar Cane and orange	Herbicide diuron (3-(3,4-dichloro-phenyl.-1,1) dimethylurea	Temperature: 50, 80, 100, 120 and 150 °C; pressure: 70, 100, 150, and 200 bar. Methanol, hexane and acetone were used as modifier	48.9–100.5%	[138]
Rice	22 pesticides (γ-HCH, chlorothalonil, vinclozolin, procymidone, p,p'-DDE, p,p'-DDT, captafol, iprodione, bromopropylate, permethrin, deltamethrin, etc.)	Temperature: 40, 50, and 60 °C; pressure: 101–404 bar; florisil, celite, extrelut, hydromatrix, and an aminopropyl material were used as fat-retention materials; volume of CO_2: 15 ml. Methanol was used as the modifier	0–94% depends on the pesticides used	[139]
Radix Astragali	Organochlorine pesticides	Pressure: 150°bar; temperature: 60 °C; the extracting time last for 10 min with the flow speed of 55 kg/h	87.6%	[140]
Passiflora alata Dryander and Passiflora edulis Sims. f. flavicarpa Deg. leaves	Malathion, methidathion, fenitrothion, fenthion, parathion-ethyl, parathion-methyl, lindane, hexachlorobenzene, chlorothalonil, tetradifon, α-endosulfan, β-endosulfan and dieldrin	Temperature: 40 °C; density of CO_2: 0.62 g/ml; pressure: 100 bar, 5 min static + 10 min dynamic	69.8–107.1%	[141]
Angelica sinensis	12 organochlorine pesticides (α, β, γ and δ-benzene hexachloride, pentachloro-nitrobenzene, pentachloroanilin, heptachlor, etc.)	Temperature: 60°; pressure: 150 bar; extraction time 20 min; CO_2 flow rate 1.5 ml/min	82.41–98.44%	[142]
Strawberries	Aldrin, dichloran, dieldrin, p,p¢-DDE (TDE), p,p¢-DDD, p,p¢-DDT, R-endosulfan, β-endosulfan, endosulfan sulfate, diazinon, dichlorvos, ethion, malathion, methyl parathion, methyl pirimiphos, mevinphos E + Z, and parathion	Temperature 50 °C; pressure 275 bar; extraction time 20 min; volume of CO_2 used 20–30 ml	74–126% (with the exception of iprodione)	[143]
Glycyrrhizae radix	13 organochlorine pesticides	Temperature: 50 °C; pressure: 252.5 bar; 5 min static extraction; 20 min dynamic extraction	78–121%	[144]

More recently, SFE technology has also been adopted for analysis of organophosphorus residue quantity in wheat and maize [147]. An automated supercritical extraction apparatus combined by solid-phase extraction using graphitized carbon black for clean-up was developed. Recoveries were at least as good as or better than, those obtained using liquid extraction (LE) and gel permeation chromatography (GPC) for 10 OPP's spiked at levels equivalent to 0.05 and 0.50 μg/g.

6. Extraction of hazardous substances from animal tissues and food

Persistent organohalogenated compounds such as brominated flame retardants (BFRs), polychlorinated biphenyls (PCBs) and organochlorinated pesticides (OCPs) have captivated worldwide concern due to their toxicology, persistence and ubiquitous occurrence in the environment. These compounds are lipophilic in nature, and thanks to their persistence and lipophilic properties, they are enabling themselves to accumulate along the food chains [148]. When these hazardous compounds enter the food chains, the analysis and removal of these contaminants are usually difficult and time consuming. Lately, Rodil et al. [148] generated multicriteria optimization of a simultaneous SFE and clean-up procedure for the determination of persistent organohalogenated pollutants in aquaculture samples. Fractional factorial design was chosen as criteria to screen the significant extraction parameters, and similar to those of most supercritical extraction studies the factors selected were extraction temperature, pressure, static extraction time, dynamic extraction time and carbon dioxide flow rate. In this work, authors make use of two reference materials in addition to fish feed and shellfish samples to validate the feasibility of their technique for analyzing organohalogenated pollutant in aquaculture.

Since decades ago, the utilization of synthetic antimicrobial agents as active agents against Gram-negative and Gram-positive bacteria in human and veterinary medicine has been widely recognized and practiced. In poultry industries, these compounds are supplemented to control Salmonella and other microorganisms. Improper use of synthetic antimicrobial agents tends to cause problematic issues. More recently, the presence of residues can be found in poultry products which increase the exposure level of its consumer with unnecessary antimicrobial compounds [149,150]. Long-term exposure of these compounds to human could cause allergic reactions, antibiotic resistant, human illness, etc. In these reports, SFE has again being utilized and affirmed as a reliable method for the analysis of the antimicrobial agents in poultry product, i.e. eggs [149,150]. In conventional practice, detachment of these compounds from eggs was hindered by significant binding between lipoprotein matrices of eggs and antimicrobial substances. Nevertheless, by using supercritical fluid lipid and protein matrices can be isolated easily while the residue of interest is removed.

OCPs are known as toxic and carcinogenic materials. A possible risk to human health can be associated with the incidental intake of its residues in food by consumers. Thus, it is necessary to separate its residual contaminants in food. These compounds are classified as first target residual contaminants as they are still widely used in many countries. Furthermore, OCPs possess a long half-life, high accumulation, potentially harmful biological effects, and detrimental impacts on the environment [142]. Several researchers detected the existence of residual OCPs within eggs [151,152]. The efficacy of SFE for the recovery of 16 common OCPs from liquid whole eggs was investigated by Fiddler et al. [151]. Supercritical carbon dioxide (scCO$_2$) without any solvent modifier is utilized to minimize interfering coextractives. The extraction condition used in their experiment was pressure of 680 bar, temperature of 40 °C, CO$_2$ flow

rate of 3.0 l/min, and extraction time of 40 min. Recovery experiments were carried out on homogenized eggs fortified at the 0.05, 0.10, and 0.20 ppm levels. At the lowest level of 0.05 ppm, recoveries ranged from 81.8% to 108.3%, with coefficient of variations (CVs) <9.8%. Another similar study was also conducted by Wigfield et al. [152].

In addition to OCPs, herbicides can also be detected within eggs. SFE study of several herbicides from fortified and incurred eggs has been reported by Pensabene et al. [153]. In their study they used different type of herbicides widely applied on animal feed crops. The herbicides were extracted from eggs fortified at 100 ppb using unmodified supercritical CO$_2$ at a pressure of 10,000 psi and a temperature of 50 °C with off-line collection on a solid phase extraction cartridge containing florisil. Atrazine recovery is averaged at 90.4% with an R.S.D. of 3.3%. The other triazines were recovered at mean levels >73%.

In general, supercritical carbon dioxide extraction methods as adopted for analysis of pesticide residues in foods are faster, simpler, less expensive, and environmentally safer than conventional solvent-based methods. SFE has been evaluated for the extraction of 17 organohalogen and organophosphate pesticides in gazpacho (a table-ready food composite containing crude vegetables, white bread, vegetable oil, water, and other minor components) using anhydrous magnesium sulfate as drying agent [154]. It is concluded that the recoveries of non-polar organohalogen pesticides were poorer than the polar pesticides and the results indicate that the SFE could also be used to determine pesticide residue level in food.It is interesting to note that SFE has also been employed to investigate the quantity of pesticide residue inside honeybees, a particular type of insects. As a member of the insect in the Hymenoptera order, its role in the human and natural world can be reflected through honey and beeswax production, aside from its assistance for pollination of a vast number of food crops. Application of pesticide for plant protection often gives harmful implication to honeybees. Jones and McCoy [155] created supercritical extraction method for analyzing organophosphate and carbamate insecticides in honeybees. SFE was deemed suitable for the routine extraction of organophosphate and carbamate insecticides from honeybees.

Another complementary study on the SFE of hazardous substances from animal tissue was performed by Antunes et al. [156]. PCBs, p,p'-DDE, p,p'-DDD, p,p'-DDT and dieldrin were extracted from fillets of black scabbardfish (aphanopus carbo). Optimum operating pressure and temperature were determined using the statistical method of central composite surface design. The studied temperature spans from 309 to 337 K with pressure from 10 to 24 MPa. They claimed that in some cases, the concentration of organochlorine compounds obtained by this method was higher than those obtained from soxhlet extraction using hexane as solvent.

7. Extraction from other solids

In the past, regeneration of activated carbon was done mostly by thermal process which requires cost-intensive gas stream cleaning in couple with particulate removal processes. Now, this extra cost together with undesirable carbon loss is avoidable through the application of SFE. The implementation of supercritical fluid technology for regeneration of activated carbon loaded with organic compounds, also called as supercritical desorption has been started since late 1980's. Table 5 summarizes various organic compounds that have been used as solutes.

Tan and Liou [157,158,162,163] conducted some research in regeneration of activated carbon loaded with benzene, toluene, and ethyl acetate using supercritical carbon dioxide. In their study, the

Table 5
Organic compounds used in supercritical desorption/regeneration of activated carbon

Compound	Investigator	Compound	Investigator
Benzene	Tan and Liou [157,158], Chihara et al. [159]	Phenanthrene	Tomasko et al. [160], Madras et al. [167,110]
2-Chlorophenol	Tomasko et al. [160,161]	Toluene	Tan and Lious [157,158], Chihara et al. [159], Tomasko et al. [160]
Ethyl acetate	Tan and Liou [162,163], Srinivasan et al. [164,165]	o-Xylene	Chihara et al. [159]
DDT	Tomasko et al. [161], Magnaughton and Foster [166]	p-Xylene	Chihara et al. [159]
1,2-Dimethylnaphthalene	Chihara et al. [159]	m-xylene	Benkhedda et al. [169]
Hexachlorobenzene	Madras et al. [167,110]	Dibenzofuran	Tomasko et al. [160]
Naphthalene	Madras et al. [167,110]	Fluorenone	Tomasko et al. [160]
Pentachlorophenol	Madras et al. [167,110]	Acridine	Tomasko et al. [160]
Phenol	Chihara et al. [159], Yeo and Kim [168]		

regeneration of activated carbon using supercritical process had more satisfactory regeneration result as compared to steam regeneration. The effects of pressure and temperatures on regeneration efficiency were examined as well, of which higher pressure condition was deemed more favorable for regeneration.

Supercritical CO_2-assisted regeneration of granular activated carbon F-400 filled with several organics compounds was carried out by Chihara et al. [159]. They evaluated adsorption equilibrium and dynamics of these organics under supercritical conditions. Benzene, o-xylene, p-xylene, toluene, phenol, and 1,2-dimethylnaphthalene were tested as injected compounds. The adsorption equilibrium constants of the organic compounds used in their study varied in accordance to their boiling point and carbon dioxide density.

Tomasko et al. [160,161] tested regeneration of granular activated carbon loaded with 2-chlorophenol, DDT and several organic compounds. The ability of SFE to extract the contaminant compounds from granular activated carbon and subsequently detach most of the contaminant into a liquid phase was studied in a pilot-plant scale apparatus was established here to study the capability of SFE to extract these compounds and subsequently release them into liquid phase. Almost all of 2-chlorophenol can be entirely removed at 40 °C and 101 bar while only 55% of the initial DDT is removed at 40 °C and 200 bar. For the other compounds about 85% removals was observed.

Srinivasan et al. [164,165] scrutinized the supercritical desorption of ethyl acetate from activated carbon as a function of CO_2 flow rate, pressure, temperature, and particle size. They carried out the supercritical regeneration process on a shallow bed of carbon with thickness of 2 mm. In their first experiment [164], low loading of ethyl acetate, in the range of a linear adsorption is applied. The linear adsorption rate is written as

$$\frac{dC_s}{dt} = k'_a \left(C_i - \frac{C_s}{K} \right) \tag{12}$$

Later on, they also studied the effect of loading on desorption rates [165]. Fig. 4 depicts the experimental concentration histories of ethyl acetate in the effluent for different loading. At low loading (11.7% and 17%), the quantities desorbed increase proportionally with loading after which a deviation from linear adsorption behavior, e.g. from Eq. (12) as loading escalates happens.

Naphthalene, phenanthrene, hexachlorobenzene, and pentachlorophenol SFE from activated carbon at 308 and 318 K and 100 atm was performed by Madras et al. [167,110]. The principle of frontal analysis chromatography is employed to determine adsorption isotherms and desorption profiles of the organics on activated carbon. Their analysis reveals the fact that the amount of organic adsorbed on carbon was independent of their organic nature. It is emphasized in their study that the regenerability of activated carbon was not always only related to the solubility of the compounds used in supercritical carbon dioxide.
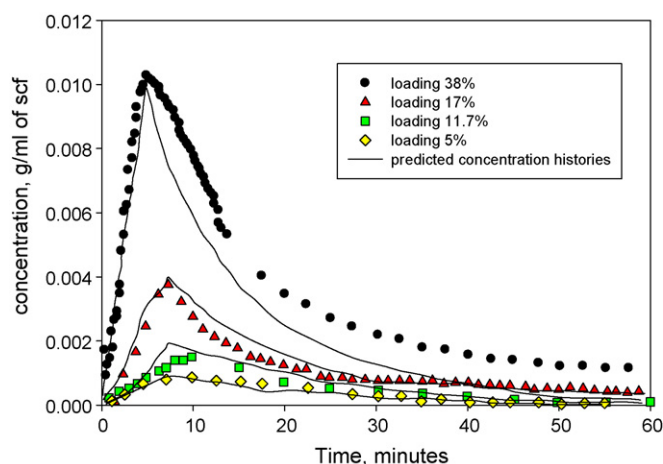

Fig. 4. Predicted and experimental concentration histories for regeneration of ethyl acetate for different loading. Adapted from ref. [165].

Supercritical adsorption and desorption behavior of DDT on activated carbon in the presence of carbon dioxide was examined by Macnaughton and Foster [166]. They aimed to obtain a greater understanding of dynamic extraction behavior of DDT from activated carbon using supercritical CO_2. Their adsorption and desorption experiments were carried out at 313.1 and 318.1 K using a fixed carbon dioxide density of 0.658 g/cm³. They found that desorption efficiency for this system escalates with both temperature and density, and the data indicated that the adsorption equilibrium at low CO_2 flow rate is the limiting transfer step.

Glaser and Shulman [170] studied the extraction of four solvents from three different adsorbents. Toluene and isooctane were extracted from a synthetic carbon, Anasorb 747; 1-butanol from silica gel; and 2-nitropropane from a porous organic polymer, Anasorb 727. They use the mode of extraction, temperature, pressure, and contact time of the supercritical fluid/sorbent as the extraction parameters.

The extraction of polar triazine herbicides from two different solid matrixes of C_{18}-silica and soil using supercritical CO_2 was carried out by Papilloud and Haerdi [171]. The optimum condition for removal of this compound from spiked C_{18}-silica was at 250 bar and 50 °C, while for soil sample was at 300 bar and 65 °C.

Clays have potential application as adsorbent to remove organic compounds from wastewater due to its low cost, high surface area, and natural availability. To improve its adsorption properties, clays can be modified by the exchange of organic cations for the inorganic cations of Ca^{2+}, Na^+ which usually occur on the internal or external surfaces of clays. Despite the significant growth in the number of studies attesting the high capacity of organically modified clays in adsorbing organic compounds, its commercial application remains scarcely observed. The main difficulty for the commercialization lies on the regeneration process. Several studies on the regenera-
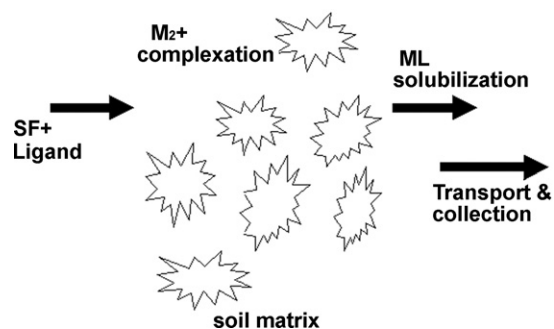
Fig. 5. Proposed mechanism for supercritical extraction of heavy metals in environmental matrices. Adapted from ref. [185].

tion of organoclays loaded with hazardous organic substances have been conducted in the recent years [172–177]. The results showed that the supercritical technology in combination with organoclays can lead to a significant saving in both adsorbent and regeneration costs.

8. Heavy metals removal

A few numbers of reviews about removal of metals from aqueous solution that make use of SFE technology have been pioneered by Erkey [178] and Wai and Wang [179]. Erkey's review incorporates 70 articles published between 1940 and 1999. On the other hand, the review by Wai and Wang comprises 61 articles published from 1951 to 1997. More than a few aspects of supercritical extraction of metals from liquids such as thermodynamics of extraction, solubility of metal complexes, distribution of molecules, reactions, effect of operating conditions, etc. have been well-presented in these reviews [178,179]. Since both of these summaries are already comprehensive, to complement them in here we only condense the studies of heavy metals removal (from liquids or solids) as published between 2000 and 2007.

Removal of heavy metals from solid matrices and liquid remain acts as a great challenge over recent years. Although, various methods are available for this purpose, again SFE seems to be more promising. Supercritical fluids modified by the addition of complexing agents have been utilized extensively for the extraction of metal ions from various solid and liquid matrices [180–195]. This distinct approach for SFE of metals is achieved by converting charged metal ions into neutral metal chelates using organic chelating agents dissolved in supercritical CO_2. The selection of suitable chelating agents is critical in the chelation-SFE of metal ions. Ideally, selected chelating agents are required to have high stability constants of the metal complexes, high solubilities of the chelating agents and their metal complexes in pure or modified supercritical carbon dioxide, fast chelation kinetics, and complexing specificity to allow selective extraction of a metal ion or a group of metal ions.

The complexing agents used in conventional solvent extraction processes can also be used in SFE complexation of metal ions, provided that they are soluble in supercritical CO_2. Solubilities of metal complexes in supercritical CO_2 vary significantly depending on the chemical nature of the complexes. Numerous chelating or complexing agents have been employed in supercritical extraction of heavy metals such as diisooctyl-thiophospinic acid (Cyanex 302), sodium diethylthiocarbamate (Aliquat 336), bis(2-ethylhexyl)phosphoric acid), bis(2-ethylhexyl)monothiophosphoric acid, etc. Mechanism of supercritical extraction of heavy metals involving chelating agent in solid matrices has been proposed by Elshani et al. [185] as illustrated in Fig. 5.

In the supercritical extraction of heavy metals, the amount or concentration of chelating agents, temperature, pressure and extraction time plays an essential role on the recovery of metals [183–188,190,193]. The amount of chelating agent/ligand must be adequate to complex all the metal ions in the sample while the chelating agent should be able to access the heavy metal sample [185]. Yet, in real condition, heavy metals generally available in environment samples within trace amount. At the same time, the complexity of the environmental matrices might add difficulties in accessing it. By increasing the temperature of the system at a certain value of pressure, vapor pressure of the solute will also increase, while on the other side the density of the supercritical fluid tends to decrease gradually with temperature as indicated in Fig. 2. As such, the trade-off exists here for the best overall parameters and the optimum condition between two opposing factors needs to be sought. Table 6 summarizes the operating conditions of the supercritical extraction studies of heavy metals [181–190,192–195].

9. Prospective use of supercritical fluid extraction—ionic liquid system for separation of hazardous substances

Albeit the fact that ionic liquids (ILs), i.e. salts that are liquids at room temperature was discovered in 1914, only more recently they start to get significant attention, especially as solvent in combination with supercritical fluid in chemical processes and separation [10]. One of the challenges in the use of ILs is the difficulties to separate the product/solute from solvent. Due to its negligible vapor pressure, inexplosive and recyclable nature, ILs are called as green solvent. On top of that, it is also possible to fine tune the chemical and physical properties of ILs by changing anion–cation combination to dissolve any certain type of solutes [10]. The possibility of applying SFE method to extract the products/solutes from ILs has been explored in the last few years. Some studies have shown that $scCO_2$ is highly soluble in most ILs while ILs are relatively not soluble in $scCO_2$ [196,197]. It is obvious that non-polar $scCO_2$ is simply incapable of solvating ion. However, with addition of polar organic compounds, ILs can dramatically dissolve $scCO_2$ [198].

Earlier, Brennecke's research group [199,200] verified that a wide variety of organic products, including hazardous substances can be extracted from IL [bmim][PF6] with $scCO_2$ at 40 °C and 138 bar with recovery greater than 95%. Non-polar organic compounds are easily extracted as compared to polar solutes. Other studies on the solubility of organic compounds focusing into fluid phase equilibria involving ILs and $scCO_2$ were recently summarized by Keskin et al. [10]. $scCO_2$ can also be applied for extraction of heavy metal from IL. Mekki et al. [201] studied the extraction of Cu^{2+} from a room temperature IL (rtIL) using fluorinated β-diketones at pressure of 150 atm and temperatures of 40 and 50 °C. The stoichiometric ratio of Cu, complexing ligand and IL in their study were 1:2:3. Without modifier addition, high extraction efficiencies can readily be achieved. Here, the underlying structure of rtIL 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide under $scCO_2$ phase was considered favorable for the carbon dioxide molecules to penetrate easily into the interstices and therefore allows extraction of CO_2 philic complexes formed by trifluoroacetylacetonate hydrate and hexafluoroacetylacetonate hydrate. In addition, the extraction of lanthanides from aqueous solution using rtIL has also been conducted [202].

As mentioned by Keskin that many studies had dealt with combination of IL and $scCO_2$ for extraction purpose. However, the applications of this combination "green" solvents for remediation from contaminated solid matrices is very scarce, only one study performed by Keskin et al. [203] can be found in the literature.

Table 6
Supercritical extraction of heavy metals

Sample	Heavy metals	Chelating agents	Pressure (bar)	Temperature (K)	Other parameters	Reference
Water	Zn	Cyanex 302	83–138	313	Ligand to metal ratio: 13:1, extraction time: 0–30 min	[181]
Fly ash and sand	Zn, Cu, Pb, Cd, and Cr	Cyanex 302, Aliquat 336, D_2EHPA, DiOPA	80–200	318	Methanol as entrainer, extraction time: 10–40 min, water concentration in matrix: 5% and 10%	[182]
CCA treated wood	Cu, Cr, and As	Acetylacetone	147	423.2	CO_2 flow rates: 0.18–0.4 mol/min, extraction time: 0–350 min, mixing ratio between ligand and CO_2: 2.1, 4.2, and 9.7 AA/mol CO_2	[183]
Polymers with multiple ligand sites	Cu, Eu	–	140	298	Ligand to metal ratio: 1:1 and 2.7:1	[184]
Sea sand and soil	Cu, Pb, Cd, and Zn	Cyanex 301, Cyanex 302, Cyanex 272, Kelex 100	101–404	313 and 333	Extraction time: 0–100 min	[185]
Municipal waste incinerator fly ash	Zn, Pb, Cu, Sb, Ni, and Cd	Cyanex 302, D_2EHPA	200	313	Ratio between ligand and CO_2: 0.006–0.02 for Cyanex 302 and 0.005 for D_2EHPA, extraction time: 45–95 min	[186]
Water and sand	Cd, Co, Cu, Pb, Zn, As, and Cr	Et2NH2DDC, NaDDC, APDC, LiFDDC, Cyanex 302	202	333	Extraction time 20 min in dynamic mode, methanol used as modifier	[187]
Acidic solutions	Hg, Cu, Cd, Pb, Zn, As, Sb, Se.	Cyanex 301, Cyanex 302, D_2EHTPA	303	333	Extraction time: 30 min in dynamic mode	[188]
Fly ash	Zn, Pb, Mn, Cd, Cu, V, Sb, Ni, Mo, Cr, and Co	Cyanex 302, TBP, D2EHPA	200	313	CO_2 flow rate: 8–18 kg/h, extraction time: 60 min	[189,190]
Soil and river sludge	CU, Pb, Zn, Cd, Cr, Ni, Co	8-Hydroquinoline (8-HQ)	150	323	Extraction time: 15 min in dynamic mode, methanol used as modifier	[192]
CCA wood	Cu, Cr, As	Cyanex 302, AA, thenoyltrifluoroacetone (TTA), trioctylphosphine oxide (TOPO), tri-*n*-octylmethyl ammonium chloride (Aliquat 336)	200–240	313–343	1 ml water added to extraction cell, effect of pH also studied	[193]
Urban total suspended particles	Cu, Pb, Zn, Cd, Cr, and Ni	H2Dz, 8-HOx, and NaDDTC	150–350	313–353	Dynamic extraction time (10–60 min), methanol used as modifier	[194]
Acid washed sea sand	Cd, Cu, Pb, and Zn	Sodium diethyldithiocarbamate (NaDDC) and dibutylammonium dibutyldithiocarbamate (DBDC)	101, 202, 303, and 404	318 and 333	Dynamic extraction was carried out with a flow rate of 1.5 ml/min for 20 min, methanol was used as modifier	[195]

Naphthalene was used as the model component to represent a group of soil contaminants and 1-*n*-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF6] was utilized as the IL. The supercritical extraction was carried out at 25, 35, 40 °C and 80, 100, 120, 140 bar conditions for 2, 4 and 6 h extraction times. They claimed that the consolidation of these two "green" solvents is promising for recovery of contaminated environment matrices in the near future.

10. Modeling of equilibrium and dynamics in supercritical extraction of hazardous substances

Adsorption and desorption processes under supercritical condition have been studied over a period of almost three decades. However, both equilibrium data and dynamic parameters, which are required for the design of supercritical adsorption or desorption processes are still necessary. One way to study the SFE process in detail includes the development of mathematical models and their application to experimental data. In this section, the static and dynamic supercritical adsorption/desorption models that have been developed so far will be discussed.

10.1. Adsorption/desorption equilibrium

Supercritical extraction of organic contaminants from dry solids such as soil, adsorbents, etc., involves two different phenomena occurring simultaneously. The organic contaminant on the solid surface can exist in two states, the adsorbed state and the deposited state. The portion of the organic that is deposited as a separate phase on the solid surface is extracted by simple dissolution in the supercritical phase. On the other hand, the extraction of the portion of the organic that is adsorbed on the solid phase is likely to be controlled by adsorption/desorption equilibrium [204].

At the equilibrium condition, the distribution of solute between the supercritical phase and solid phase can be determined by the adsorption isotherm. There are a number of adsorption isotherm equations that can be used to correlate supercritical adsorption/desorption equilibrium data, and the most widely used are Langmuir [98,164–166,169,175,205] and Freundlich [21,85,96,110,164–166,206] isotherm equations. Langmuir isotherm equation has the form of

$$q^* = \frac{q_0^* K' C_e^*}{1 + K' C_e^*} \tag{13}$$

while Freundlich has the form of

$$q^* = q_0^* (C_e^*)^{1/n} \tag{14}$$

Other available alternative isotherms are the linear adsorption isotherm [162,163], BET model [21], Toth equation [160,207], and Dubinin–Astakhov [208] equation.

Adsorption and desorption processes of naphthalene, phenanthrene, hexachlorobenzene and pentachlorophenol from activated carbon in the presence of supercritical carbon dioxide were studied by Madras et al. [167,110]. In their reports, adsorption/desorption isotherms of these compounds were successfully modeled using Freundlich isotherm. Fig. 6 shows the adsorption isotherm of hexachlorobenzene on activated carbon at 308 K and 113 atm.

Macnaughton and Foster [166] have obtained the adsorption and desorption isotherm of the priority pollutant DDT on activated carbon at 313.1 and 318.1 K with a fixed carbon dioxide density of 0.658 g/cm³. The equilibrium data can be described well by Freundlich model. Freundlich equation was also used to describe the supercritical phenanthrene desorption isotherms from five dry soil materials [206]. Operating conditions of the measurements were at 40–60 °C and 120–310 atm. They found that the Freundlich equation is capable to adequately describe all of 40 isotherms obtained.
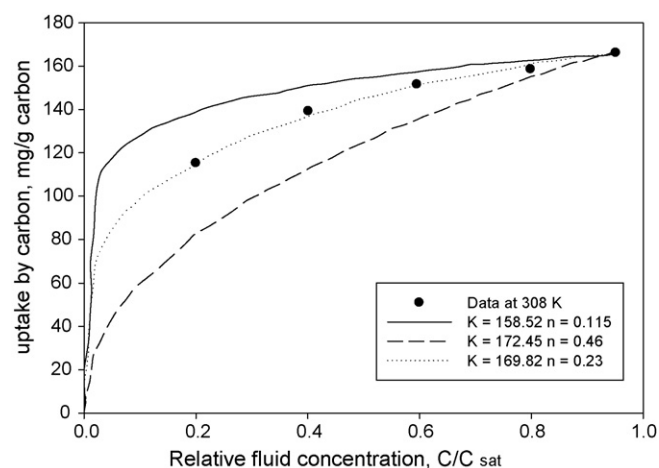

Fig. 6. Adsorption isotherm of hexachlorobenzene on carbon at 308 K and 113 atm with various values of *K* and *n*. Adapted from ref. [167].

Supercritical extraction of phenol and 4-nitrophenol from organically modified smectite was performed by Park and Yeo [175]. They investigated the desorption characteristic of phenols at three different temperatures and pressures up to 420 bar. The adsorption/desorption isotherms of these compounds were well-presented by the Langmuir model.

Dubinin–Asthakov equation, which is widely used to describe gas and liquid phase adsorption isotherm, has also been used to describe the adsorption equilibrium in supercritical condition. Dubinin–Astakhov (DA) equation has the following form

$$q^* = q_0^* \exp\left[-\left(\frac{RT \ln(P'/P_s)}{E'}\right)^n\right] \tag{15}$$

Shojibara et al. [208] used the Dubinin–Astakhov equation to correlate their adsorption equilibrium of benzene on activated carbon in the presence of supercritical carbon dioxide. The saturation capacity, q_0^*, was found to decrease with the increasing pressure. At constant temperature, as the pressure increases, the density of the carbon dioxide will escalate leading to the intensified solubility of the solute in the supercritical fluid. Thus, the amount of solute adsorbed in activated carbon will also be reduced. On the other hand, with the density increase, the amount of CO_2 adsorbed will also be increased. Adsorption isotherms of benzene on BPL activated carbon under supercritical condition are shown in Fig. 7. From this figure, it can be seen that at the supercritical condition (7.94 and 11.87 MPa), the amount of benzene adsorbed in activated carbon increases with temperature rise. At the pressure below crossover region, the density of supercritical CO_2 decreases with the increas-
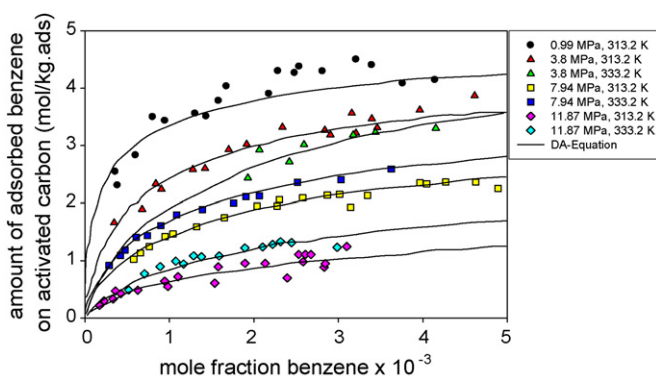

Fig. 7. Adsorption isotherms of benzene on BPL carbon. Adapted from ref. [208].

ing temperature; therefore, the solubility of solute in supercritical fluid also decreases, which causes the increase of the amount of solute in solid phase.

10.2. Mathematical modeling in dynamic mode

Mathematical modeling of the supercritical extraction process kinetics is also required in order to gain a better understanding of the systems and the phenomena involved in the process. Supercritical extraction process involves several complex phenomena, some of which are very difficult to be described precisely through mathematic models. Therefore, almost all mathematical models available in the literature have several simplifying assumptions applied to the basic physical model, assumed as best as possible to describe the actual phenomena. There are several classifications of the existing SFE models. The classifications of supercritical extraction models available in the literature are essentially the same. None of the available models in the literature can be used as a universal model since the supercritical extraction process handle many different type of host matrices from different source, in which the characteristic and physical properties are extremely different.

Different assumptions were used to develop the SFE model from solid matrices such as linear desorption kinetics, neglecting the axial dispersion, linear driving force concept and neglecting mass transfer effect. Most of the available models have been developed with the assumption of negligible axial dispersion, constant solvent density and flow rate along the particle bed [25,91,98,157,158,168,173–176]. The general mass balance based on the above hypothesis can be written as:

$$u\frac{\delta C}{\delta z} + \theta\frac{\delta C}{\delta t} + (1-\theta)\frac{\delta q}{\delta t} = 0 \tag{16}$$

The initial boundary conditions for Eq. (16) follow

$$t = 0, \quad C = 0 \tag{17}$$

$$z = 0, \quad C = 0 \tag{18}$$

If the desorption process is assumed as an irreversible and first-order (linear desorption kinetics) [25,158,168,173–176], therefore the term of $\delta q/\delta t$ follows

$$\frac{\delta q}{\delta t} = -k_d q \tag{19}$$

with the initial condition

$$t = 0, \quad q = q_o \tag{20}$$

Recasens et al. [209] proposed an isothermal model for supercritical desorption of ethyl acetate on activated carbon. The effect of axial dispersion, external and intraparticle mass transfer, and non-linear kinetics on overall desorption rates were also taken into account in the model. They assumed that the adsorbent particles are spherical and the local adsorption isotherm is following the non-linear Langmuir equation. The mass conservation in the void region can be written as

$$\theta\frac{\delta C}{\delta t} + u\frac{\delta C}{\delta z} = \phi\frac{\delta^2 C}{\delta z^2} - \frac{3(1-\theta)k_m}{r_0}\left[C - (C_i)_{r=r_0}\right] \tag{21}$$

The mass balance in the pores follows

$$\gamma\frac{\delta C_i}{\delta t} = D_e\frac{1}{r^2}\frac{\delta}{\delta r}\left(r^2\frac{\delta C_i}{\delta r}\right) - \rho k_a(C_m - C_a)C_i + \rho k_d C_a \tag{22}$$

The mass conservation on the solid particles was written in the following Langmuirian form

$$\frac{\delta C_a}{\delta t} = k_a(C_m - C_a)C_i - k_d C_a \tag{23}$$

Their model well-describe the experimental data of Tan and Liou [157].

Model based on thermodynamic and kinetic approach was also used by Kubatova et al. [92] to describe the mechanism which control the extraction of polycyclic aromatic hydrocarbon from historically contaminated soil with hot water and supercritical carbon dioxide. A simple thermodynamic model based on single distribution coefficient (K_D) is rendered satisfactory enough. This model assumed that the kinetics of the initial desorption step and subsequent fluid-matrix partitioning are rapid, and thus did not significantly affect the extraction rate. The shape of extraction curve was defined by:

$$\frac{S_b}{S_0} = \frac{(1 - S_a/S_0)}{(K_D m/((V_b - V_a)d) + 1)} + \frac{S_a}{S_0} \tag{24}$$

It can be seen that Eq. (24) only relies on the volume of extractant used since this model does not contain extraction time parameter. Hence, doubling the extraction fluid flow logically will double the extraction rate versus time. They also used a simple two-site kinetic model consists of two first-order expression

$$\frac{S_t}{S_0} = 1 - (F e^{-k_1 t}) - (1 - F)e^{-k_2 t} \tag{25}$$

Eq. (25) relies solely on time. The results of their study indicate that simple thermodynamic and kinetic models can also provide the direction of parameters in developing extraction conditions.

Another model for supercritical desorption of various organic from solid matrices was proposed by Madras et al. [110]. They proposed a model without the used of any adjustable parameters, and they used the following assumption:

- isothermal system;
- radial concentration gradients are neglected;
- constant physical properties of the fluid;
- axially dispersed flow pattern;
- local equilibrium exists in the pores.

Orthogonal collocation using finite elements method is utilized to solve the partial differential equations involved in the model. Their model can predict the experimental data quite well.

11. Conclusions and perspectives

This works aims to summarize and discuss representative information and advances associated with supercritical technology exploitation in hazardous substances analysis and recovery. A great number of condensed data have been presented to provide clearer pictures in many specific applications involved.

In spite of great efforts accumulated for improving the supercritical extraction for decontamination of multitude hazardous compounds, its commercial applications is still only a panacea. However, the future of this technology can be regarded as bright, especially with the advancement of readily coupled "green" technology such as ionic liquids which tends to complements the application area inaccessible before by only supercritical fluid technology.

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