Supercritical extraction of contaminants from soils and sediments

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Abstract

This paper summarizes representative developments in the field of polluted soil/sediment decontamination by supercritical extraction (SCE). The broad accomplishments of SCE through sustained research and its applications as a remedial technology are outlined. This technology basically employs green supercritical fluids (SCFs) such as carbon dioxide (SCCD) and water (SCW) for the extraction of volatile organic compounds (VOCs) and persistent organic pollutants (POPs), which include polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and various pesticides from environmental matrices. Comprehensive data on solute solubilities in SCFs, partition equilibrium of solutes between a solid matrix and SCFs, solute desorption from the matrix, and solute separation from the SCF provide a solid basis to develop models regarding a SCE process. Significant experimental results and various proposed models to interpret the extraction phenomena from soils/sediments are presented. SCE has been developed to be applied as an environmental remedial technology after its successful use in analytical chemistry. This development has occurred because of a need for a rapid, safe and cheap cleanup method. Conventional techniques for the extraction of environmental matrices (e.g. liquid solvent extraction, thermal desorption) are time and solvent/energy consuming. The review attempts to summarize the representative studies about SCE of organic contaminants, advantages and the drawbacks of SCE compared to other remedial technologies, and economic aspects. A short section on the future direction for research in this field and general trends toward commercial applications are also included.

This review is also intended as a guide for conducting a remediation study in a systematic and stepwise fashion for determination of the effectiveness of SCE technology in conjunction with other cleanup technologies. Systematically conducted and well-documented remedial studies are important in the investigation/feasibility and design processes. The applicability and inherent limitations of SCE technology to determine its specific suitability are also discussed.

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1. Introduction

Last century legacy of rapidly developing and changing technologies and industrial products and practices frequently generated inappropriate disposal and spill of harmful materials threatening both public health and the environment. Soil/sediment contamination by VOCs and POPs including PCBs, PAHs, DDT, dioxins and furans, pesticides, etc., is still of a significant concern. Currently there are few economically and technically practicable technologies for the treatment of various soils/sediments contaminated by plethora of chemicals at wide levels of contamination. Conventional techniques such as thermal desorption, incineration and liquid solvent extraction are expensive and involve risks associated with air and residual pollution.

The SCE technology largely has built on knowledge acquired on the use of SCFs for extracting organic compounds from solid matrices for analytical work. Early efforts in the field of environmental SCE focused on studies associated with using SCCD to extract a wide variety of harmful chemicals from spiked soil/sediment samples. The next step was to demonstrate the feasibility of the new technology using contaminated soils and sediments collected from various sites as real-world/native contaminated samples.

Due to research efforts over the last decades, soil/sediment cleanup using SCE processes is a technique available nowadays. Dr. Akgerman pioneered and carried out extensive work in the field of environmental SCE [1–22]. His critical reviews [1–6], scientific articles [7–22], numerous communications at national and international conferences, seminars, research reports, etc. have been gratefully appreciated by the scientific community. He was the first to use tracer response techniques (both pulse and step inputs) to determine equilibrium and kinetic parameters for SCE of contaminants from soils and activated carbon.
Comprehensive presentations of various aspects on SCFs used in solute extraction from environmental matrices are provided in books [23–27], critical reviews [1–6, 28–35], numerous articles, master and doctoral theses, research reports, etc. Although SCE has also applications as a treatment technology for inorganic contaminants, this review is focused on extraction of organic compounds. The reviews outlined procedures used for inorganic contaminants, this review is focused on extraction.

2. A brief technology description

The remediation technologies can be classified into three major treatment types: biological, physical/chemical, and thermal. SCE is included in the second category as a subcategory of solvent extraction. The SCF is chosen such that it has a higher affinity for contaminants than for the bulk material of the solid matrix. Most of the SCE processes use SCCD ($T_{cr} = 31^\circ C; P_{cr} = 74$ bar) individually or mixed with cosolvents (entrainers; modifiers) from which the most common is methanol ($T_{cr} = 239^\circ C; P_{cr} = 81$ bar). SCE uses the enticing SCF properties (i.e. liquid-like density, low viscosity, high diffusivity, and no surface tension) to extract contaminants at optimum temperature, pressure, and flow rate conditions. Rather than destroying in situ pollutants at relatively low concentrations with significant energy and/or materials just to be absorbed by the bulk matrix, the SCE process is a first step of two- or multi-step remedial technologies. SCE does destroy neither contaminants, nor the soil/sediment. The extracted pollutants are highly concentrated and can be subsequently destroyed more cost effectively. All SCE processes for remediation purposes employ similar unit operations including feed preparation, extraction, separation of solids and solvent, and recovery of the solvent.

2.1. Pre-treatment

A pre-treatment step is frequently required for SCE systems. It consists of soil/sediment preparation for an optimal SCE process. The rocks, roots, and other debris are removed and the water content adjusted appropriately. Other characteristics of the soils/sediments may be also adjusted (e.g. pH, chemical composition).

2.2. Treatment

Environmental SCE removes the organics from contaminated solids followed by solute–solvent separation and solvent recycle (Fig. 1). In the SCE step, excavated solids are placed in a pressure vessel and extracted with a recirculated stream of SCFs, which are well mixed with the contaminated matrix to allow contaminants to transfer to the solvent. The clean matrix, the solvent, and the solute(s) are then separated by physical methods. Following extraction and separation, organic contaminants are subjected to a suitable destruction technology while the clean solvent is recycled to the extraction stage. The soils/sediments are not significantly affected by a SCE process and can be returned to the natural site.

2.3. Post-treatment

SCE is not a stand-alone technology. The concentrated contaminants and any separated cosolvent and water are typically subject to further specific treatment and disposal techniques, as appropriate, to complete the cleanup (Fig. 1). Side streams generated during treatment, such as spent solvent/cosolvent, spent activated carbon, air emissions, etc., must also be treated. However, SCE systems are contained and designed to operate without air emissions.

3. Solubility studies

Any project on SCE is planned to provide engineering design information to develop this process to remediate contaminated soils/sediments. For example, a process conceptual analysis at Syracuse University revealed that multidisciplinary studies of
solute solubility in SCFs, partition equilibrium, and laboratory- and bench-scale desorption were needed to accomplish the proposed objective [36–45]. Original laboratory equipment was designed, constructed, commissioned, and used to carry out experiments for all of these fields of interest.

The solubility data permit one to assess the most desirable SCF from capacity and selectivity standpoints. Solute solubility in a SCF depends on many factors such as solute and SCF structure and thermodynamic properties (i.e. polarity and polarizability, critical point $T$–$P$ values, vapor pressure, etc.), specific solute–SCF interactions, etc. The main factors that affect the solubility are considered to be solute vapor pressure and SCF density. Solubility level of a solute in a SCF provides the limit of the amount of the solute that can be extracted at saturation equilibrium.

Basically, two different approaches have been used to acquire solubility data of various solutes in SCFs: static and dynamic methods [23]. To overcome the main disadvantages of the conventional methods, a new quasi-static technique [36] was recently proposed, being classified between the static and dynamic methods. A very slow SCF flow rate does not significantly disturb thermodynamic equilibrium of the solute–SCF–matrix of subsequent states but permits the acquisition of a high number of solubility data-points in a short time (several tens per isotherm).

An extensive solubility data for solids in SCFs has been acquired by various methods since the naphthalene solubility in SCCD has been first studied [7,8,23,36–38,46–51]. Successful (semi)empirical correlations were proposed for the data of solute solubilities over the experimental conditions [36–38,52,53]. However, accurate models to predict rather than correlate experimental values of different solute solubilities in various SCFs are still desired [54].

4. Partition equilibria

A key piece of information for the modeling, optimization, and design of a SCE process to remediate polluted soil/sediments is the partition equilibrium data of solutes between SCFs and environmental matrices. Partition equilibrium models and experimental data have been reported for several solutes in systems with SCCD and a liquid or solid phase (mainly water or activated carbon). These compounds include 2,4-dichlorophenol [14], phenol [55–57], $p$-chlorophenol, $m$-cresol, and benzene [57], toluene [58], a PAH mixture [15], naphthalene, phenanthrene, hexachlorobenzene, and pentachlorophenol [10,13,16]. Partitioning isotherms are also reported for the solutes pentachlorophenol, 2,3,4,5-tetrachlorophenol and 2,4-dichlorophenoxyacetic acid between water and SCCD at about 40°C and 100–270 bar [59].

The partition equilibrium data of various POPs between SCCD and different types of soil are also available [9,60–62]. In these studies, the quantity of the solute extracted by SCCD and the quantity remaining in the soil were measured and used to calculate the partition coefficient for each compound. The distribution coefficients for phenol between soil and SCCD were measured at 24–76°C and 90–300 bar and the effects of soil organic content, soil moisture, temperature, and pressures were investigated [17]. Thermodynamic models were developed for temperature and pressure dependency of the distribution coefficients. Methanol was tested as an entrainer and experiments were conducted with C6H6 to investigate the effects of co-pollutants. The results showed that the presence in the system of chemicals other than PhOH affected the distribution coefficients.

PCB partition equilibrium studies between SCCD and three real-world St. Lawrence River sediments with similar properties and PCB congener distribution patterns but different total
PCB concentrations were conducted at 50 °C and 76–178 bar (five different SCF densities) [39]. The data were analyzed for both total PCBs and 12 major individual congeners detected in the sediments. The results were used to model PCB desorption rates. All the isotherms showed good linearity except for those at lower density (5.5 and 8.0 mol/L) in SCCD system. Preferential desorption was found among the PCB congeners analyzed. The partition coefficients increased roughly with the molecular weight of PCB congeners. The increase of either temperature or density while keeping one of them constant resulted in the decrease of partition coefficients (favoring PCB desorption) for both SCCD and SCCD–MeOH fluids. Temperature and density effects appeared to be more significant for the CO₂–MeOH system than for pure CO₂.

Based on the characteristics of the experimental isotherms, a simple linear model has been employed to characterize PCB partition equilibrium data:

\[ q = K(\rho, T)C \]  

where \( q \) (ppm) and \( C \) (μg/mol) are PCB equilibrium concentrations in the sediments and SCF, respectively. The PCB partition equilibrium coefficient, \( K (\text{mol/g}) \), is a function of supercritical fluid density and temperature. The values of \( K \) were determined for each isotherm through linear regression. The correlation between the partition coefficients (\( K \)) and system temperature and pressure was established for each PCB–sediment–SCF system. These models have been used in the analysis of PCB desorption data. The model analysis revealed that PCB adsorption onto sediments from both SCFs were exothermic and physical processes. Marine sediment, diesel soot, and air particulate matter showed the effectiveness of SCE as a technology for the cleanup of PCB contaminated soils/sediments under 30 min of extraction at 40 °C and 101 bar as more than 90% of PCBs in river sediments were removed. The extraction of PCBs from spiked samples showed even higher efficiencies. In another example, the effects of temperature and pressure on recovery of SCE were studied [63]. SCE conditions using SCCD at 40–150 °C were developed to allow sequential extraction of PCBs associated with rapidly desorbing, moderately, slowly, and very slowly desorbing sites on polluted sediments and soils [64]. The results demonstrated that the sample matrix and not PCB identity was most important in controlling desorption behavior.

SCE rates of both spiked and native PCDDs and PAHs from different environmental samples were examined at constant fluid density and flow rate [65]. The reported results showed increasing the SCE temperature as an effective method to increase SCE rates. Marine sediment, diesel soot, and air particulate matter were extracted with SCCD at 405 bar or modified CO₂ at 80 and 200 °C for 15 min of static followed by 15 min of dynamic SCE [66]. An increase in PAH recoveries was observed for all three samples by raising the temperature from 80 to 200 °C, which demonstrated that the temperature enhancement was independent of the sample matrix.

Decreasing the polarity of water by sequentially raising the temperature to 400 °C (SCW, if \( P > 221 \) bar) allowed class-selective aqueous extractions of polar (e.g. chlorinated phenols), low-polarity (e.g. PAHs), and non-polar (alkanes) organics to be performed [67]. To quantify the effects of temperature and pressure on SCE, certified materials (e.g. PCBs from river sediment, PAHs from urban air particulate matter, and PAHs from highly contaminated soil) were extracted with pure CO₂ at conventional (50 °C) and high (200 °C) temperatures [68]. At 50 °C, raising the extraction pressure (355–659 bar) had no effect on extraction efficiencies. However, PCBs from sediment and PAHs from air particulates were efficiently extracted only if the temperature was raised to 200 °C. At 200 °C, PCBs were effec-
tively extracted at any pressure while both higher temperature and pressure increased the recovery of PAHs from air particulates. These results showed that temperature was more important than pressure for achieving high extraction efficiencies when the interactions between pollutant and sample matrices are strong.

5.1.2. Nature of the SCF and cosolvent (entrainer) effect

Although there is no definite theory that enables one to select a modifier for SCE, it appears that modifiers should be selected using both matrix and target solute characteristics. The reported SCE data show that small amount of a cosolvent (up to 15%) enhance SCE recovery for specific solutes. The most important property of a cosolvent is considered its polarity.

The modifier effects were dependent on the sample matrix and modifier identity when environmental samples were extracted with SCCD alone and modified with 10 vol.% MeOH, diethylamine, or toluene [66]. The effects in recoveries with high temperature and modifier were additive, indicating that temperature and modifiers have different mechanisms of improving solute recoveries. SCE recoveries for in situ pollutants including PCBs from sediment and PAHs from a petroleum waste sludge and railroad bed soil were compared using SC CHClF₂, diethylamine, or toluene [66]. The effects of various water contents on thermodynamic and kinetic parameters of the SCE process were measured using different matrices. The reported results for a naphthalene-contaminated loamy sand [74, 75] showed that SCCD easily extracted naphthalene from soil when the water content was below 10%. At low water contents, mass transfer was therefore limited primarily by the desorption/kinetic process [73]. The extraction rates controlled primarily by the solubility/elution process showed direct correlation with SCE flow rates while the extraction rates for samples that are controlled primarily by the kinetics of the initial desorption step showed little or no change with different SCE flow rates. Even similar samples can show different types of behavior. For example, the extraction rates of many PAHs from a highly contaminated soil depend heavily on SCE flow rate and are therefore limited primarily by the solubility/elution step, while the extraction rates of the same PAHs on a less contaminated soil show little or no dependence on flow rate and are therefore limited primarily by the desorption/kinetic step. Samples limited by the solubility/elution step are extracted most efficiently using dynamic SCE, while samples limited by the desorption/kinetic step are efficiently extracted using either static or dynamic SCE.

5.1.3. Flow rate

SCF flow rate showed important effects on both solute desorption rate and final residual concentrations. The effect of flow rate on SCE rates has been used to determine whether the extraction is limited primarily by analyze solubility and retention of analytes on matrix active sites (i.e. the solubility/elution process) or by the desorption/kinetic process [73]. The extraction rates controlled primarily by the solubility/elution process showed direct correlation with SCE flow rates while the extraction rates for samples that are controlled primarily by the kinetics of the initial desorption step showed little or no change with different SCE flow rates. Even similar samples can show different types of behavior. For example, the extraction rates of many PAHs from a highly contaminated soil depend heavily on SCE flow rate and are therefore limited primarily by the solubility/elution step, while the extraction rates of the same PAHs on a less contaminated soil show little or no dependence on flow rate and are therefore limited primarily by the desorption/kinetic step. Samples limited by the solubility/elution step are extracted most efficiently using dynamic SCE, while samples limited by the desorption/kinetic step are efficiently extracted using either static or dynamic SCE.

5.1.4. Water content

Water has a significant influence on the SCE of organics from solid matrices, even for low natural water content [19, 45, 74, 75]. The water content of the samples and the presence of cosolvent were the most important factors affecting desorption of PCBs from sediments [45]. These solutes are more tightly bound in real-world than in spiked samples. Although the role and the mechanism of water effects on SCE are still controversial, the reported data point to the fact that a small amount of water, <5%, may increase the rate of SCE. Water contents <10% showed no signs of significant mass transfer limitations. However, at >20% water, mass transfer was ~10 times slower than at water contents of <10%. When phenol was extracted from dry and wet soil contaminated with 1 wt.% PhOH using SCCD [19], it was concluded that soil moisture had a major impact on the effectiveness of entrainers for soil SCE.

The effects of various water contents on thermodynamic and kinetic parameters of the SCE process were measured using different matrices. The reported results for a naphthalene-contaminated loamy sand [74, 75] showed that SCCD easily extracted naphthalene from soil when the water content was below 10%. At low water contents, mass transfer is rapid and the equilibrium partition coefficient is independent of the water content of the soil. However, the overall mass transfer coefficient decreased by a factor of ~200 when the water content increased from 10 to 20%.
5.2. Mechanisms of SCE processes and modeling

A reliable design of a SCE unit requires the ability to model the experimental data and knowledge of the mechanisms involved in SCE processes. Following is a short presentation of the research activity on these aspects.

5.2.1. Adsorption/desorption mechanisms

Numerous studies were conducted to determine the adsorption and desorption characteristics of organic compounds in different soil/sediment samples. The results showed that the Freundlich isotherm satisfactorily represented adsorption and desorption of dissolved TCE in these media [76]. A study has been carried out to provide basic information on the mechanisms associated with sorption and desorption of PCBs on and from contaminated sediments by using SCE with SCCD [77]. The extracted PCBs were then spiked into water with the parent sediment for 18 days. The selective SCE conditions developed earlier were used to determine the proportion of PCBs, which could be extracted under conditions of increasing stringency. It was found that 18 days was not sufficient time for PCBs to migrate to the slower sediment-binding sites, which the PCBs had occupied in the real world sediments and that the adsorbed PCBs were primarily associated with the binding sites most easily extracted by SCE.

Benzene, toluene, ethylbenzene, o-, m-, and p-xylene (BTEX), and PAHs were extracted from eight soils from sites that had been abandoned for several decades [78]. Benzene was generally the slowest compound to be extracted from all samples. Since the solubility of benzene in SCCD is higher than the solubilities of PAHs, these results demonstrated that benzene was more tightly sequestered than toluene, ethylbenzene, xylenes, or the multi-ring PAHs. Removal rates of PAHs from polluted soils were determined using water desorption for 2–120 days and mild SCE with SCCD for 20–40 min [79]. Water and SCE profiles were fit with a simple two-site (fast and slow) model to obtain the fraction of each PAH that was rapidly released. The comparisons with bioremediation indicated that short-time SCE provided a reasonable estimation of the fraction of PAHs readily released and available for microbial treatment.

SCE processes for the recovery of organic pollutants from environmental samples require three main steps: partitioning of the targeted solutes from the sample into SCF, removal from the extraction vessel, and collection of the extracted compounds. While spike recovery studies are an excellent method to develop selective SCE technology toward upscale applications. Solute desorption from a fixed bed of sediments can be modeled employing the transient desorption material balance and assuming negligible axial dispersion effects. The governing equation can be written as:

\[
\varepsilon \frac{\partial C}{\partial t} + u \frac{\partial C}{\partial z} + (1 - \varepsilon)\rho_p \frac{\partial q}{\partial t} = 0
\]

where \(\varepsilon\) is void fraction of the soil bed; \(C\) is the solute concentration in the SCF phase; \(t\) is processing time; \(u\) is SCF superficial velocity; \(z\) is axial dimension of the bed; \(\rho_p\) is the density of soils/sediments; and \(q\) is solid phase solute concentration. A linear relationship (1) can relate the partition equilibrium of the solutes between SCF and solid phase, and the solute diffusion rate is governed by a linear driving force:

\[
\frac{\partial q}{\partial t} = \frac{15D_s}{R_p^2}(KC - q)
\]

where \(R_p\) is the soil particle radius and \(D_s\) is a “lumped” diffusion coefficient for the solutes. Combined with Eqs. (1) and (3) and a set of initial and boundary conditions, Eq. (2) can be solved and the parameters \(D_s\) and \(K\) determined by regression analysis on the experimental desorption data when partition equilibrium data are not available for \(K\) values. This model was used, for example, to fit PCB desorption data from sediments and spiked till under various conditions [40,77]. The parameters obtained from laboratory-scale desorption data predicted the bench-scale
The desorption profiles of other various organics from soil using SCFs were also modeled [11,18,21]. The models accounted for effective diffusion of the organics in the solid pores, axial dispersion in the fluid phase, and external mass transfer to the fluid phase from the particle surface. The systems of partial differential equations were solved, for example, using the orthogonal collocation on finite elements. The results predicted the experimental data quite well without any adjustable parameters. Adsorption equilibrium and the effective pore diffusion of the organics were considered among the most significant parameters in all the systems investigated. The axial dispersion coefficient of hexachlorobenzene in SCCD was investigated by on-line chromatography with pulse-response experiments, which indicated that this coefficient was a function of temperature, pressure, and flow rate [21]. The results suggested that the contribution by convection was more important than diffusion under SC conditions.

Three kinetic models for the SCE of contaminants from soil [83] considered the axial dispersion, particle-to-fluid mass transfer coefficient, intraparticle diffusion and the equilibrium partition coefficient as main factors affecting the extraction. The first three of these factors affected the shape of a breakthrough curve while the latter affected the breakthrough time. The models have been applied to literature breakthrough data to determine parameter values necessary to fit the observations.

A simple diffusion model has been used to fit the selective SCE profiles obtained in [64] for PCBs in the real-world contaminated sediments and soils [84]. The model considered spherical and planar geometry and was extended to describe the influence of increasing temperature during the extraction. Diffusion was considered to be an activated process with the diffusion coefficients dependent on the temperature according to the Arrhenius equation. The model with spherical geometry was fitted to all matrices to estimate diffusion coefficients and activation energies. These data correlated well with relevant literature values obtained from long-term water desorption experiments, indicating that it might be possible to replace these experiments with rapid SCE to predict the rate of release of pollutants under field conditions.

A four-step model for dynamic SCE was also proposed: rapid SCF entry into the matrix, a reversible release process, solute transport by diffusion to the edge of a matrix particle, and removal by solvation in the fluid [85]. It can explain the sequential kinetic features of dynamic SCE: a slow initial extraction followed by a more rapid extraction phase, and a slow final phase. The model can be used to estimate the values of the parameters quantifying the individual steps.

A kinetic model including terms for matrix-SCF mass transport, partitioning, and bulk mass transport in the SCF was used to distinguish between SCE processes with spiked and native analytes [65]. Desorption experiments suggested that a model should include external and intra-particle mass transfer and be based upon equilibrium at a desorption site. A model including the effects of both solvation by the SCF and diffusion out of the matrix was developed for dynamic SCE [86]. The model was consistent with many of the features of experimental evidence. An idealized model was also suggested for the analysis of SCE results for a flow system by a SCF from a matrix containing small quantities of extractable materials, such that the extraction was not limited by solubility [87]. The model considered solute diffusion out of a homogeneous spherical particle into a medium infinitely diluted. The effects of matrix shape/size and solubility limitations on the model were discussed.

Successful strategies for quantitative removal of contaminants from soils by SCE require the development of adsorption–desorption profiles using available mechanistic and modeling tools. Various models to interpret and predict the extraction phenomena from solid matrices of solute mixtures were proposed with emphasis on the fundamental parameters like adsorption equilibrium constants, mass-transfer coefficients, axial dispersion coefficients, and effective diffusivities of the solutes in the matrix pores [18,20,21]. Local equilibrium theory was found to predict the desorption profiles fairly accurately for the desorption of naphthalene, phenanthrene, hexachlorobenzene, pentachlorophenol, and VOCs from soil using SCCD [10,18]. A model was proposed for the prediction of adsorption and desorption profiles of VOCs from oven-dried soil in a packed-bed column [18]. The model assumed local equilibrium between the pore gas phase and the solid phase in the soil, axially dispersed flow pattern in the column, and mass transfer resistances in the particle and in the film around the particle. If the initial soil loadings of the VOCs exceeded a certain limit, the desorption breakthrough profiles exhibited a plateau section linked to the existence of a desorption hysteresis. Similarly, two types of the continuously and the stepwise decreasing profiles of chlorinated compounds were observed for the vapor extraction from soil [20,21]. Desorption profiles were linked to the shape of the adsorption isotherms and showed a two-step behavior. The first step corresponded to desorption along the desorption branch of the isotherm, and the second step corresponded to desorption along the adsorption isotherm after the hysteresis closure. The second step was the rate-controlling step for the overall desorption process. Although the SCE phenomena are complex, the predictions for the targeted solute mixtures were considered successful.

### 5.3. How accurate are SCE data from different sources?

SCE processes are so complex that reproducible results at different laboratories (often in the same laboratory) are difficult to be obtained. An inter-laboratory study of SCE of PAHs from soil samples to assess this reproducibility was conducted [88]. Three laboratories participated in the study by extracting three real-world samples in triplicate. The samples were extracted at 355 bar and 90 °C for 20 min in the dynamic mode with SCCD at a flow-rate of 1.0–1.5 mL/min. The extracted material was collected in 10 mL dichloromethane and analyzed chromatographically. The SCE method accuracy (percent recovery) was determined relative to the sonication extraction since the true levels of PAHs in these samples are not known. The PAHs with concentrations >1 mg/kg were recovered >80% by SCE. The inter-laboratory method precisions were concentration-dependent.
The errors were <27% and 19–80% for concentrations above and below 1 mg/kg, respectively. From these results, the authors concluded that the method appeared quite rugged and the inter-laboratory data compared well with other SCE inter-laboratory studies.

5.4. Bench-, pilot-, and commercial-scale SCE

In the most cases, small-scale SCE data do not translate in a reliable design for commercial applications and scale-up experiments are crucial. However, follow-up experiments conducted with a 2 L fixed bed bench scale unit confirmed the laboratory scale findings for the extraction and destruction of PCBs from contaminated sediments [43,44]. Results of laboratory- and bench-scale investigations indicated that SCCD–5% MeOH is an effective SCF and conditions have been defined to achieve sub 5 ppm PCB residual concentration in 45–60 min for 99.8% removal. Comprehensive data on PCB solubilities in SCCD/MeOH, partition equilibrium, and desorption provided a solid basis to scale-up the extraction step of these processes. Further, the SCW oxidation (SCWO) stage, coupled to the SCE process with three possible configurations, seemed to provide clean effluent materials (Fig. 1). The ultimate products of the proposed technology were mainly clean soil/sediments and inorganic species such as H2O, CO2, and small amounts of chlorides. The SCWO studies indicated that 5245 ppm Aroclor 1248 in methanol-simulated soil extracted solutions can be oxidized to 99.95% conversion in less than 1 min at 550 °C.

A two-step process using SCE with SCCD and wet air oxidation of the extracted contaminants in solid matrices has also been proposed [89]. SCE tests are conducted over wide ranges of temperature, pressure, and CO2/contaminant ratios with PAH polluted soils. The addition of methanol as a modifier was studied. At comparable CO2-to-contaminant ratios and extraction conditions of 48 °C and 139 bar, the total PAHs removed from the three soils were 76.9–97.9% with CO2 alone and 88.4–98.6% with methanol added. A skid-mounted field test unit based on the laboratory bench-scale test results was constructed which allowed on-site testing of the integrated SELPhOx process with contaminated soils.

Bench-scale study results from SCE of soil polluted with naphthalene and 1,2,4-tri-Me benzene as a function of the SCCD flow rate and density have been reported [90]. Data were used to perform a basic economic analysis of the process and to develop scale-up methodology from laboratory-scale SCE devices to industrially useful equipment. Laboratory scale data such as mass transfer coefficients can affect the sizing and the control of process units since high mass transfer rates allow smaller vessels. This study also included experimental data collection and analysis to support the application of SCE and to provide design and operational processes required to construct a pilot plant unit. A preliminary economic analysis using these results showed that the proposed SCE process is feasible.

Soil polluted with hydrocarbons from a petrochemical plant was treated to reduce the pollution level below legal limits by a pilot-scale SCE unit [91,92]. This pilot plant for soil remediation with SCCD and subsequent adsorption of pollutants on activated carbon has been used to study scale-up procedure for SCE processes. Operational parameters (e.g. extraction temperature, solid particle size, solvent ratio) were optimized and the results showed an optimal extraction temperature of 40 °C, particle size of 0.425 mm, and solvent ratio of 15.8 kg CO2/kg soil h. Increasing the temperature improved initial extraction rates and total recovery while pollutant solubility in the SCF did not limit SCE. Diffusion into the SCCD phase was the extraction rate limiting step. The effect of particle size was particularly strong for short time spiked soil in the laboratory. The data have also been used to obtain the mass transfer coefficients and the equilibrium parameter using a desorption model. From the results obtained in pilot plant, the design of a mobile full-scale plant has been developed and the following data were obtained: soil treatment capacity of 250 kg/h under 260 bar and 40 °C extraction conditions; adsorption conditions of 260 bar and 50 °C; gasoil concentration of 14,500 ppm; SCCD flow of 452 kg/h; extractor of 270 L (three extractors in series of 90 L per extractor and one extractor more for semi-continuous operation); extraction time of 84 min per shift.

Results of bench scale SCE of diesel, PCB, and bis(2-ethylhexyl)phthalate (I) polluted soil and the process implication for scale-up feasibility were also reported [93]. Extractions at 69–413 bar at 25–60 °C and different solvent to feed ratios were tested. For 50 g samples, extraction efficiencies were: >99% for soil containing 45 g/kg diesel at 76 bar and 23 °C; 87% for soil containing 34 mg/kg PCBs at 96 bar and 24 °C; and 95% for soil containing 15 g/kg I at 90 bar and 24 °C. Extractions at 60 °C and 413 bar of 500 g sample reduced the same pollutant levels by >99% for diesel-polluted soil, and 97% for the PCB- and I-polluted soils.

6. Separation methods

Conclusions obtained from the above studies indicate that though this technology is highly valuable for treating specific types of soil, it is associated with relatively high cost of treatment. This is mainly due to the cost of re-compressing the SCF, which is de-pressurized to separate the solutes. The trapping efficiency can also affect the overall solute recovery in a SCE process.

Florisil and octyldecylsilane (ODS), used as trapping materials [63], both produced satisfactory recoveries (>95%) for most solutes under optimized conditions, but the performance of Florisil was less dependent on SCE flow-rate. At higher flow-rates, ODS gave lower recoveries of the chlorinated benzenes which Florisil recovered up to 95%. When pure CO2 was used at a constant flow rate, change in the SCE conditions did not significantly affect the trapping efficiency. Use of modifiers led to good recoveries with a trap temperature above the boiling point of the modifier.

Solute–SCF separation by adsorption onto activated carbon has been proposed as a solution to SCE high cost of repressurization of CO2 [13,94]. Under these conditions the plant operates in a quasi-isobaric state and, therefore, the depressurization–repressurization cycle is avoided and energy costs minimized. A pilot plant using this separation method.
was designed and built at the Chemical Engineering Department of Valladolid University [94]. Normal operating conditions included 70–300 bar and 30–70 °C for a soil load of 1 kg. For a regeneration time of 60 min, pollutant concentration was reduced to <25 mg/kg.

An isobaric method to regenerate SCCD was investigated as an alternative to customary regeneration through pressure reduction [95]. In an example of soil remediation, activated carbon regeneration of SCCD loaded with pyrene was examined. The characteristics of SCE for soil remediation were examined up to 100 °C and 300 bar. The desorption isotherms were measured first. This method was then used to regenerate CO₂ in a closed solvent-cycle plant with a 4 L extractor. An economic analysis indicated that soil remediation costs decreases by about 20–30% by means of an activated carbon adsorbent.

7. Bioavailability and toxicity of the contaminants

When speaking about environmental remediation standards, the obvious question is “how clean is clean?” The way this question is addressed has a major impact on the technology selection and the time and resources required to accomplish the cleanup task. A primary barrier, inhibiting the further development and routine use of SCE, is its inability to meet performance standards for incineration, the remedy on which regulatory standards are based. As a result, this cleanup standard has been criticized as too stringent and inadequate because it is a relative standard based on an established technology instead of risk assessment.

Based on the desorption studies on the pollutants in soils/sediments, an important fraction of these chemicals is tightly bound within the matrix sites with no or negligible bioavailability. Many pollutants become sequestrated as they age for decades in the environment. Therefore, it may be more important for an extraction method to only recover environmentally-relevant pollutant fraction, rather than conventional attempts to extract all pollutant amount regardless of how tightly bound it is to the soil or sediment matrix. For example, extremely slow desorption and limited bioaccumulation of PAHs has been reported [82,96–98]. Mild SCE with SCCD preferentially extracted bioavailable PAH molecules in soil [97] while biologically unavailable PAHs are not extracted, suggesting that SCE could be used for the removal of soil toxicity.

Information on the pollutants bound to the fast and slow sites of environmental matrices should be of great value for the determination of their bioavailability in sediments and soils, and this technique has the potential to develop into a powerful tool in environmental risk assessment [82]. A portion of POPs in soils and sediments resist desorption, extraction, and biodegradation. Understanding the mechanisms controlling this sequestration process has been elusive but it comes to light as showing by new testing methodologies relevant to the environmental bioavailability of hydrophobic organochlorines in soils and sediments [99].

8. Comparison with other technologies

The number of other remedial technologies for polluted soils and sediments is quite impressive, showing the high interest on this topic of environmental engineering. Just a few of commercial scale applications demonstrate the difficulties of the domain. Some of these technologies deal with both extraction and destruction of soil/sediment pollutants either in one or two step processes. Remedial technologies for polluted soils and sediments include incineration, thermal desorption, solvent extraction (which includes SCE), chemical remediation, and bioremediation. Some of them are in situ applications, other require soil/sediment excavation/dredging. A short presentation of the place and performance of SCE in comparison of other remedial technologies follows.

A mild SCE with SCCD for 20–40 min allowed for the fast fraction extraction values of some PAHs to be estimated and showed excellent agreement with the removal of individual PAHs obtained with 147–343 days of field bioremediation [79]. Also, extraction efficiencies obtained in 30–45 min using SC CHClF₂ generally matched or exceeded those obtained using 18–22 h liquid solvent extractions [69]. SCE with CO₂ was used for the determination of total petroleum hydrocarbons (TPH) in real-world fuel-spill soil containing heavy fuel oil, diesel fuel, light crude oil, gasoline or kerosene [100]. TPH results of SCE at 400 bar and 150 °C, were comparable or higher (up to 134%) than those obtained by Freon-113 Soxhlet extraction (4 h). In another example, extraction of PAHs from polluted soil was done with a Soxhlet apparatus (18 h), by pressurized liquid extraction (PLE) (50 min at 100 °C), SCE (1 h at 150 °C with SCCD), and subcritical water (1 h at 250 °C, or 30 min at 300 °C) [101]. Although minor differences in PAH recovery resulted from the different methods, quantitative agreement among all the methods was generally good. However, subcritical water, PLE, and Soxhlet extractions had poor selectivity for PAH versus bulk soil organic matter (~1/4 to 1/3 of bulk soil organic matter was extracted along with PAHs), while SCE removed only 8% of the bulk organic matrix. SCE comparisons of the untreated and bioremediated soils showed that bioremediation only removed PAH molecules which were found in the fast fractions by SCE and that remediation for 1 year did not result in the migration of PAHs from slower to faster sites [102]. One hour SCE of the untreated sample at the mildest condition (120 bar, 50 °C) gave good quantitative agreement with removals achieved after 1 year of bioremediation. The results show that mild SCE may be a rapid and useful test to predict the bioavailability of PAHs on contaminated soil.

Also, SCE was compared to traditional Soxhlet extraction for PCB congeners in sediments [103]. The concentrations determined using SCE compared well with the certified concentrations for the majority of the PCB congeners. A SCE analytical method to extract PCBs and PAHs from soils was demonstrated in field experiments at different waste sites and was shown to give results in excellent agreement with conventional Soxhlet extraction [104]. The limits of the method were ~200 ppb of individual PAHs and ~10 ppb of individual PCBs (~100 ppb of total PCB as Aroclor 1260). SCE with SCCD at 50, 200, and 350 °C to extract PAHs, N- and S-heterocycles, chlorinated phenols, and pesticides from a variety of soil and soot samples was directly compared to Soxhlet extraction of 18 h with identical analytical methods [105]. While SCE efficiencies at 50 °C
(30 min) typically were lower than Soxhlet (18 h) recoveries, SCE at 200 °C generally gave good quantitative agreement with Soxhlet extraction. The increase in SCE extraction efficiencies observed at 200 and 350 °C was not explained by volatility considerations alone, since thermal desorption at these temperatures did not yield recoveries as high as SCE.

The extraction efficiencies of both PCDDs/PCDFs and PCBs from sediments obtained by SCE agreed well with those obtained by the Soxhlet method [106]. The reproducibility of SCE was high for both groups. The relative extraction rates of native and spiked deuterated PAHs (d-PAHs) from environmental samples including petroleum waste sludge, urban air particulate matter, and railroad bed soil were compared using sequential extractions with pure SCCD or CO2 modified with 10 vol.% methanol and using sonication with methylene chloride [81]. Similar results were observed using SCE and conventional methylene chloride sonication.

Eleven alternative treatment technologies for PCB-contaminated sediments were compared and ranked based on technical performance, status of development, test and evaluation data needs, and cost [107]. The processes involved were: low-temperature oxidation, Cl removal, pyrolysis, concentration, vitrification, and bioremediation. All of these technologies required further development and testing.

Based on the SCE results compared to other remedial methods it is suggested that: (a) the SCE cleanup efforts should focus on the quick remediation of the heavily contaminated hot spots to eliminate the most severe risk threats and prevent further spread of pollutants into surrounding areas; and (b) the two-step removal-destruction processes seems to be a better fit for the cleanup problems of contaminated soils/sediments.

9. Economic analysis

The base case of the proposed remediation process for PCB contaminated soils/sediments using SFT technology [41] consists of three 2.5 m3 extractors operated in a 30 min cycle (the time for each extractor to be exposed to fresh SCF) and in a 60 min processing time (cycle- plus recycle-time of PCB/SCF from a previous extractor) (Fig. 1). It can treat 36,000 m3/year contaminated soils/sediments. The total processing cost for the SCE–SCWO process includes the cost for handling the solids, SCE of the PCBs, and the cost of oxidizing the extracted PCBs using SCWO. The excavation costs are estimated to be $50/m3 and the SCWO costs for the extracts are estimated to be $15/m3-sediment. Purchase costs are estimated for all of the major process units. The total operating cost is estimated from the costs of operating labor, utilities, raw materials, the fixed capital investment, soils/sediments processing, and SCWO. The total processing cost consists of the total operating cost plus the depreciation of the plant over 10 years. Capital cost factors are used for each process unit to account for installation, engineering and construction expenses, and contingency funds and fees. Appropriate cost factors are employed for utilities, materials and maintenance. Using the costs outlined above, the total treatment cost including depreciation is $175/m3 of soils/sediments for the base case.

Two alternatives to the base process were also evaluated. In the first alternative, the cycle time for the extraction of the soil is decreased from 30 to 20 min. Another extraction unit is added and each canister is exposed to CO2 and methanol for three cycles instead to two, increasing the rate of soils/sediments treatment from 5 to 7.5 m3/h. For this alternative, the capital cost is increased by the cost of the extra unit, but labor and other operating costs for the process are essentially the same. The estimated total treatment cost for this alternative is $142/m3. In the second alternative, the CO2 and methanol stream used to extract the soils/sediments is assumed to leave the extraction units at 70% of the equilibrium PCB concentration. The estimated total treatment cost for this alternative is $144/m3.

Economic analysis of the SCE step reveals that the operation costs for the proposed process are in the range of $122–154/m3 of soils/sediments. Comparison of these costs with the costs of other alternative technologies suggests that the SCE process is economically promising and attractive for the remediation of PCB contaminated soils/sediments (Table 1). More generally, for bench-, pilot-, and industrial-scale capacities, a price index formula for the cost of a SCE unit has been proposed as:

\[
P_I = A(10VQ)^{0.24}
\]

Table 1
Comparison of relevant processes for remediation of contaminated soils/sediments

<table>
<thead>
<tr>
<th>Process</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Cost ($/m^3)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Supercritical fluid extraction</td>
<td>High extraction efficiency; no second hand pollution; soil structure is left intact</td>
<td>Further treatment of the extracts; high-pressure equipment; soil excavation required</td>
<td>122–154</td>
<td>[41]</td>
</tr>
<tr>
<td>In situ thermal desorption</td>
<td>No excavation required; applicable to heterogeneous soil; broad applicability</td>
<td>Further treatment of the extracts; high temperatures; high energy; slow process</td>
<td>100–380</td>
<td>[108]</td>
</tr>
<tr>
<td>Liquid solvent extraction</td>
<td>High extraction efficiency; low T–P conditions; portability</td>
<td>Difficult solute separation; further treatment of the extracts; residual pollution</td>
<td>250–1169</td>
<td>[109]</td>
</tr>
<tr>
<td>Incineration</td>
<td>High destruction efficiency; continuous flow system; broad applicability</td>
<td>High cost and energy consumption; emission of toxic gas/ash; irreversible soil degradation</td>
<td>360</td>
<td>[110]</td>
</tr>
<tr>
<td>Bio-remediation</td>
<td>No second hand pollution; broad land applications; ambient conditions</td>
<td>Low destruction efficiency; very slow process; inactive for some solutes</td>
<td>245–474</td>
<td>[107]</td>
</tr>
</tbody>
</table>
where $A$ is a constant, $V$ is the total extractor volume and $Q$ is the design flow rate [111]. This correlation shows on a logarithmic scale that high investment costs grow slowly with the capacity. However, on the other hand, the SCE units require low operating costs, which may compensate for high investment costs.

10. Future trends

Despite great efforts and expenditure of resources to develop both technically and economically effective SCE cleanup, no widely accepted design has been found and further research is still needed. Potential methods of decontamination processes of soils/sediments seek to use multi-step remedial technologies, i.e. SCE followed by an advanced oxidative process.

In order to simplify these technologies, an attractive possibility appears by combining extraction with oxidation by using the same SCF (e.g. CO$_2$) both as extraction fluid and oxidative medium [112]. The extracted pollutants in SCCD can be oxidized with air or oxygen under similar conditions of SCWO process: 450–550°C and ~250 bar. If the pollutant concentration in the CO$_2$ extract is not high enough for auto-sustained combustion, an enrichment step can be included, or a supporting fuel added to the oxidation step (alternatively an entrainer added to the extraction acts as supporting fuel in the oxidation).

Another attractive possibility appears to use an oxidant such as O$_3$ along with the SCF to extract and oxidize the contaminants in one-step process. Experimental results obtained in the oxidation of model compounds in SCCD from high-pressure extraction of wastewater and soil and regeneration of catalysts and adsorbents with SCCD appears to support the concept of a combined extraction/oxidation process.

Unfortunately, the early laboratory research did not translate into successful commercial applications as expected. This situation rendered some scientists and potential beneficiaries skeptical about the future of the SCE environmental technology. However, the perspectives can be regarded as optimistic. For example, in the biggest environmental remediation project in U.S. history [113], some 100,000 out of 1.3 million pounds of PCBs in contaminated sediments of Hudson River will be removed and the SCE would be a suitable technology for PCB extraction.

The SCE use as a tool for environmental control and cleanup should not be seen as a panacea, but rather must be carefully chosen on a more realistic case-by-case basis. In general, highly polluted but relatively narrow spots (e.g. local spilted POPs) are the best candidates for SCE remediation. Accordingly, more rigorous and specific designs of SCE processes are needed and the information on various aspects of the phenomena associated with these processes must be more accurate. Hence, more reliable experimental data and valid models are in great demand.

Important criteria to select an appropriate soil remediation technology include costs, processing speed, equipment dimensions, and social acceptance (current desires for cleaner technologies). Although all these criteria favor the use of SCE technology, “there is yet a barrier of inertia that goes against capital expenditure on novel projects” [114]. This review is consequently also intended to signal that this barrier is somewhat artificially maintained and that a SCE process might be a better choice for a remediation technology for specific situations.

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