CONTINUOUS CLEANING OF CONTAMINATED SOILS USING IONIC LIQUIDS AND SUPERCRITICAL CO_2

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Soil pollution has become an important concern for chemical industries. Ionic liquids (ILs) and supercritical carbon dioxide ($scCO_2$) are 'green' replacements for volatile organic solvents due to their unique properties. The solubility of $scCO_2$ in IL and insolubility of IL in $scCO_2$ give a binary system which can combine advantages of two green solvents. This work investigates the feasibility of using an IL/$scCO_2$ system for separation of harmful contaminants from soil. The study aims to utilize the ability of IL to dissolve organic contaminants at near ambient conditions from soil and the ability of $scCO_2$ to recover organic contaminants from IL in order to recycle the IL. A model component, naphthalene was used to represent soil contaminants. This model component was extracted with IL, 1-Butyl 3-methylimidazolium hexafluorophosphate [bmim][PF_6]. Since $scCO_2$ is soluble in IL and naphthalene is soluble in $scCO_2$, solute extraction was performed without any cross contamination. The IL cleaned by $scCO_2$ treatment can then be recycled. The process suggested permits the use of continuous processing of the IL-contaminant-$scCO_2$ system at high pressures in contrast to some earlier suggestions.

INTRODUCTION

Soil pollution has become an important environmental problem in the world due to industrialization. The soil contaminants threaten healths of plants, animals and humans as well as an essential natural source; water. The contaminants can pollute the underground water by leakage through the soil or they may pollute the surface water sources by erosion. A wide range of technologies are used for the remediation of contaminated soil, including the technologies based on liquid extraction. In order to extract the contaminants from soils, volatile organic solvents such as toluene, benzene, methanol etc. are used. Traditional methods, in which these organic solvents have high participation, although necessary on processing level, are significant sources of environmental pollution via fugitive emission [1]. The evaporation of organic solvents to atmosphere has a harmful effect on human health and environment.

Supercritical fluid extraction (SCFE) technologies have some advantages over the conventional liquid extraction techniques such as the ability of supercritical fluids (SCFs) to dissolve organic contaminants from soil and the ability to change the solvent power of SCFs by varying the temperature and pressure. Moreover, the high solute diffusivities in SCFs give superior mass transfer properties. SCFs are environmentally acceptable compared to volatile organic liquids. However such processes require that the contaminated soil has to be processed at high pressures, where expensive batch handling is a must.

Akgerman *et al.* [2] investigated the feasibility of extraction of hexachlorobenzene from soil by $scCO_2$. Subsequent study determined the adsorption and desorption isotherms for naphthalene, phenanthrene, hexachlorobenzene and pentachlorophenol as model components in the soil in the presence of $scCO_2$ [3]. The model components were chosen to represent the polyaromatic hydrocarbons and polychlorinated compounds which are important soil pollutants.

ILs become desirable part of environmentally benign chemical processing with unique properties such as negligible vapor pressure, low toxicity and excellent solvent power for organic, inorganic and organometallic compounds. ILs are relatively a new class of chemicals, composed of organic cations and, mostly inorganic anions. They are molten salts that are liquid at ambient conditions with melting points near or below room temperature, generally under 100ºC [4, 5, 6, 7]. They are potential replacements for organic solvents because of their non-volatility and excellent dissolution properties. The separation of products from IL is achieved with $scCO_2$. $scCO_2$ dissolves in ILs to facilitate extraction but ILs do not dissolve in CO_2, so a pure product can be recovered [8]. Therefore, non-volatile organic compounds can be extracted from ILs using $scCO_2$ which is widely used to extract large organic compounds with minimal pollution. $scCO_2$ has high volatility and low polarity whereas ILs are nonvolatile and fairly polar, therefore they are considered to be environmentally benign solvent partners.

Extraction of a solute from an IL was first introduced by Blanchard and Brennecke [8]. They have shown that $scCO_2$ can be used to quantitatively extract a relatively nonvolatile solute, naphthalene, from the IL, [bmim][PF_6]. The major advantage of this process was explained as performing the solute extraction without any cross contamination between the IL and $scCO_2$. Not only was the naphthalene extracted efficiently by $scCO_2$ but also [bmim][PF_6] was recovered in its original purity after the extraction and depressurization. Subsequent work performed demonstrated that a wide variety of solutes, including alcohols, amides, and ketones can be extracted from [bmim][PF_6] with $scCO_2$ with recovery rates greater than 95% [1].

MATERIALS AND METHODS

In this study, the materials used were 1-n-butyl-3-methlyimidazolium hexafluorophosphate ([bmim][PF_6]) (Fluka, >96 % purity) and naphthalene. All the materials were used as received. Naphthalene was chosen as the model component to represent the soil contaminant since it readily dissolves in [bmim][PF_6] and $scCO_2$. CO_2 (99.7 % pure) was supplied in cylinders equipped with dip tubes by Habaş Inc., İstanbul. Naphthalene was extracted with [bmim][PF_6] from soil and $scCO_2$ was used to recover the naphthalene from [bmim][PF_6] to recycle IL. The amount of model component extracted from soil with [bmim][PF_6] and the amount of model component recovered from [bmim][PF_6] with $scCO_2$ were measured using UV-Visible spectroscopy.

Soil Extraction: Soil was sieved and cleaned by using water, hexane and acetone in order to remove any contaminant from soil and observe the extraction of naphthalene. The maximum allowable naphthalene concentration in commercial-industrial lands was tabulated in literature as 50 µg. naphthalene in 1 g. soil [10, 11, 12]. In soil extraction experiments, 5 mg. naphthalene was added to 1 g. soil and 1.875 ± 0.1 ml. [bmim][PF_6] was used. These experiments were conducted

in a solid-liquid extraction set-up at atmospheric pressure and at 50°C. The 50°C was chosen since the solubility of naphthalene in [bmim][PF_6] is at a maximum. After [bmim][PF_6] was added, soil-naphthalene-[bmim][PF_6] mixture was stirred vigorously and the [bmim][PF_6]-naphthalene solution obtained was centrifuged (Eppendorf Centrifuge 5415C) for five minutes at 10000 min^{-1} in order to separate the soil particles which were collected during extraction. The resulting [bmim][PF_6]-naphthalene samples were analyzed using UV-Visible Spectrophotometer (Analytikjena, Specord 200) to determine the amount of naphthalene extracted from soil.

Some of [bmim][PF_6] was absorbed by the soil at the end of the soil extraction and not released. Acetone (Merc, >99 % purity) was used to recover the remaining [bmim][PF_6] from soil. Acetone-[bmim][PF_6] mixture was heated to 70°C evaporate acetone and recover [bmim][PF_6] (Since IL has no vapor pressure, it does not evaporate). The mass balance of the system was satisfied by checking the amount of [bmim][PF_6] recovered after soil extraction, the amount of [bmim][PF_6] recovered after washing the soil with acetone and the amount of [bmim][PF_6] used at the beginning of the experiment. In this study, acetone, a volatile organic solvent was used to recover the absorbed IL from soil since [bmim][PF_6] is not miscible with water. If a hydrophilic IL is chosen for the process, remaining IL can be easily recovered with water.

$scCO_2$ Extraction: The feasibility of using $scCO_2$ to recover the naphthalene dissolved in [bmim][PF_6] was investigated. $scCO_2$ extraction experiments were conducted at 35 and 40°C and 100, 120 and 140 bar. These experiments were performed in a high pressure stainless steel cell. The volume of the cell was 230 cm^3, having 12 cm height, 8 cm OD and 6 cm ID. The cell had a bolted type head with two inlets and was manufactured from 316 SS. The cell and its valves were capable to withstand pressures up to 200 bar. To keep the cell and its contents at constant temperature, the high pressure cell was immersed in a constant temperature water bath that was equipped with a thermostat (Heto Instruments) of 0.1°C accuracy. The walls of the constant temperature water bath were made of 8 mm thick glass. [bmim][PF_6]-naphthalene solution was placed into high pressure cell with glass bottles, having 4.3 cm height, 1.5 cm ID.

A gas cylinder with a dip-tube attachment at a pressure of 60 bar at 15°C was used to supply CO_2 to the high pressure cell. In the experimental set-up, a drier (silica gel bed, 6.15 cm ID and 25 cm length) removed the water vapor that might be present in the commercial grade CO_2. The gas was then cooled to -12.5°C in refrigerated bath (Heto, CB7) containing water/monoethylene glycol mixture so that the moisture of CO_2 was kept below the atmospheric pressure and probable gasification was prevented before entering the diaphragm pump (Lewa, type EK). Liquid CO_2 was then compressed to the desired operating pressure by the diaphragm pump, the head of which was also cooled by the circulated refrigerant. After compression, CO_2 was introduced into a surge tank (6.15 cm ID and 25 cm length) to dampen the fluctuations generated by the pump. In order to maintain a constant pressure within the system, a hand adjustable back-pressure regulator with a stated accuracy ± 1 per cent of the relief pressure range (Tescom Co.) was used. The experimental set-up used is depicted in Figure1.

[bmim][PF_6]-naphthalene solution obtained after soil extraction was placed into high pressure cell with glass bottle. The cell was submerged into the constant temperature water bath and connected to the system. Before CO_2 was pumped, the cell stayed in the water bath for a

sufficient time in order to adjust the cell temperature. After the thermal equilibrium was reached, CO_2 was pumped to the system. Since the solubility of CO_2 in [bmim][PF_6] is affected by the water vapor dissolved in [bmim][PF_6], the air inside the cell must be removed. When the cell pressure reached 15-20 bar, the inlet valve V2 was closed and the valves V3 and V5 were opened to discharge the high pressure cell to ensure that no air remained in the cell and CO_2 was again pumped to the desired pressure. The cell and its contents were contacted with CO_2 for 4 hours at specified temperature and pressures. After this period was over, the valves V3 and V4 were opened and the cell was discharged. The samples taken from the IL in the cell were analyzed using spectroscopy to determine how much naphthalene was extracted from [bmim][PF_6] with $scCO_2$.

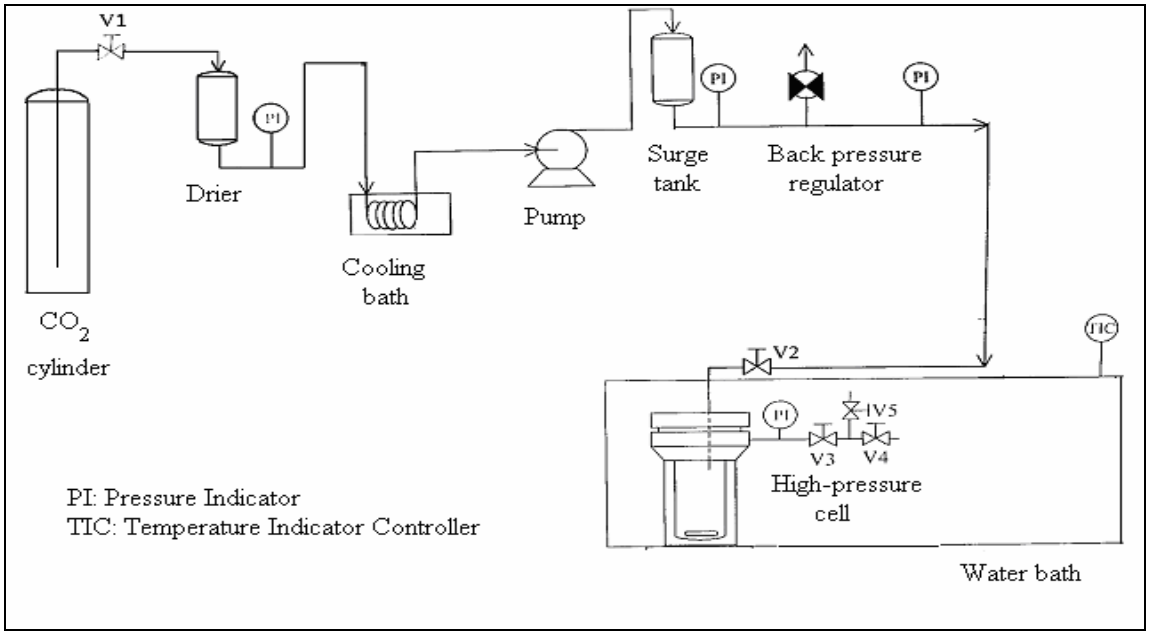


Figure 1: Experimental Set-up

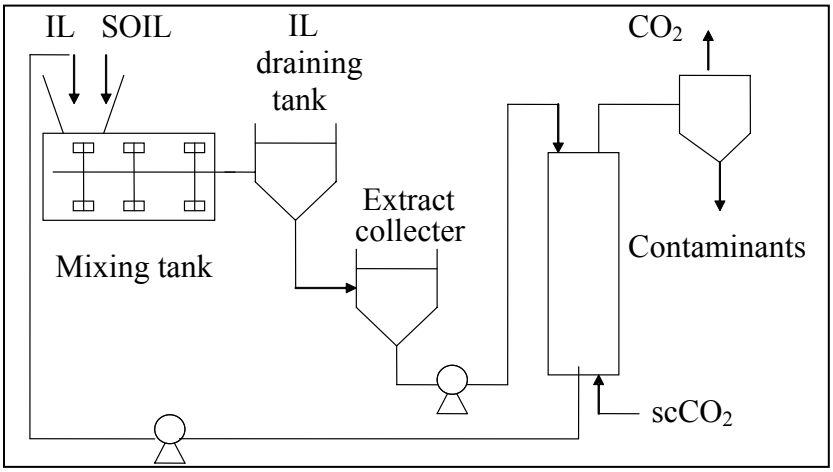


Figure 2: A Suggested Process for Continuous Cleaning of Soils Using ILs and $scCO_2$

RESULTS

Soil Extraction: At the beginning of the experiments, soil was extracted with water, acetone and hexane as explained above. However, there may be some soil constituents which are not soluble in these solvents but soluble in [bmim][PF_6]. In order to eliminate the effect of these solutes, soil without naphthalene was extracted with [bmim][PF_6] and the resulting solution was used as blank solution. Then, soil with naphthalene was extracted with [bmim][PF_6] and the resulting sample was compared with blank solution. All the samples were analyzed with UV spectroscopy at 310 nm. where the absorption of naphthalene in [bmim][PF_6] was highest. Although all the soil extraction experiments were conducted at 50°C and atmospheric pressure with the same procedure, there were some differences in the amount of naphthalene extracted from soil:

Table 1: Amount of Naphthalene Extracted from Soil with [bmim][PF_6]

Experiment number	Amount of naphthalene extracted from soil with [bmim][PF_6] (g)	Naphthalene remained in soil (μg)	Results (Limit: 50 μg)
1	0.004979	20.74	below the limit
2	0.004292	708.36	not below the limit
3	0.004956	43.66	below the limit
4	0.004933	66.58	not below the limit
5	0.004956	43.66	below the limit
6	0.004979	20.74	below the limit

$scCO_2$ Extraction: The goal of this work was not only to clean the soil with [bmim][PF_6] but also to recycle IL. The preliminary experiments showed that absorbance of pure [bmim][PF_6] decreases slightly after contacting with $scCO_2$. In order to eliminate the effect of $scCO_2$ on the absorbance of [bmim][PF_6], pure [bmim][PF_6] was extracted with $scCO_2$ and the resulting solution was used as blank for these experiments. Then, [bmim][PF_6]-naphthalene solution was extracted with $scCO_2$ and the resulting sample was compared with blank solution. All the samples were analyzed with spectroscopy at 310 nm.

Table 2: Amount of Naphthalene Extracted from [bmim][PF_6] with $scCO_2$

Experiment number	$scCO_2$ extraction P (bar)	T (°C)	Amount of naphthalene extracted from [bmim][PF_6] with $scCO_2$(g)	Naphthalene remained in [bmim][PF_6] (g)
1	140	40	0.004172	0.000828
2	120	40	0.003255	0.001745
3	100	40	0.001582	0.003418
4	140	35	0.003759	0.001241
5	120	35	0.003071	0.001929
6	100	35	0.001536	0.003464

In $scCO_2$ extraction experiments, the effects of temperature and pressure on the recovery of naphthalene from [bmim][PF_6] were investigated. As the pressure increases, the amount of naphthalene recovered from [bmim][PF_6] increased. Furthermore, experimental results suggest that decreasing the temperature reduces the recovery rate of naphthalene from [bmim][PF_6] as shown in Figure 3 and Table 2.

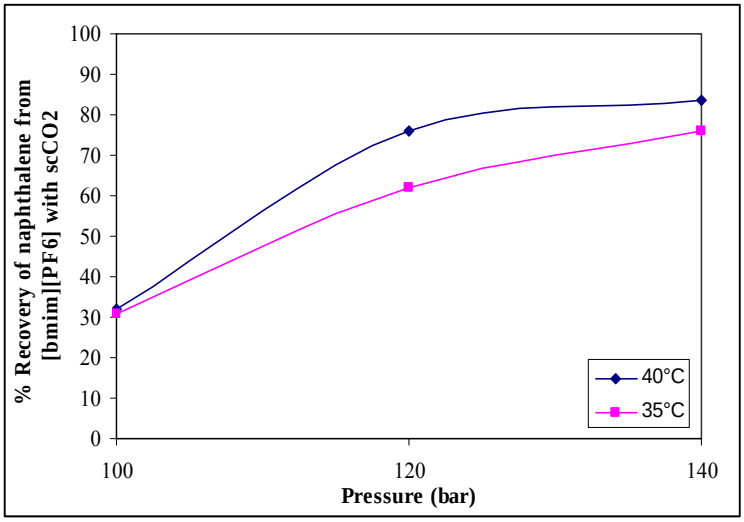


Figure 3 : Extraction of Naphthalene from [bmim][PF_6] with $scCO_2$ at 35, 40°C and at 100,120,140 bar

Table 3: Recovery of Naphthalene from [bmim][PF_6] with $scCO_2$

$scCO_2$ extraction P (bar)	T (°C)	% Recovery of naphthalene
140	40	83.78
120	40	75.84
100	40	31.91
140	35	76.19
120	35	61.97
100	35	30.84

CONCLUSION

In this study, contaminated soil was remediated with [bmim][PF_6], which is a potential replacement for harmful volatile organic solvents conventionally used because of its non-volatility and excellent dissolution properties. The model component dissolved in [bmim][PF_6] was recovered with another environmentally benign solvent, $scCO_2$ in order to recycle [bmim][PF_6]. Since the soil was cleaned near ambient conditions, suggested process permits the use of continous processing of [bmim][PF_6]-contaminant-$scCO_2$. [bmim][PF_6] and other ILs have ability to dissolve various kinds of compound, therefore this work demontrates that organic, inorganic or organometallic contaminants can be separated from soil with IL/$scCO_2$ system.

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