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Regeneration of catalyst clay soils (Tonsil CO 610 G) by supercritical carbon dioxide

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Abstract−Extraction of deactivatived materials from contaminated clay soils (Tonsil CO 610 G) by supercritical carbon dioxide was investigated. Effect of different conditions including extraction temperature (308.15-338.15 K) and pressure (100-330 bar) (thermodynamic conditions), flow rate (4.2-42.6 cc/min), and static time (45-85 min) were investigated to find the optimum conditions for extraction of deactivatived materials. Based on the different experiments, optimum conditions for flow rate (4.2 cc/min), static time (85 min) and extraction pressure and temperature (330 bar and 313.15 K) were obtained. In addition, the GC-MS analysis and Bromine index (BI) analysis were revealing that the clay soil is activated and could be used as catalyst again.

Key words: Supercritical Carbon Dioxide, Tonsil CO 610 G, Extraction, Soil Contamination, Regeneration

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 volatile organic compounds (VOCs) including polychlorinated biphenyl (PCBs), polycyclic aromatic hydrocarbons (PAHs), dichlorodiphenyltrichloroethane (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 a 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 supercritical extraction (SCE) technology largely has been built on knowledge acquired in the use of supercritical fluids (SCFs) for extracting organic compounds from solid matrices for analytical work.

In the field of extraction processes, using supercritical fluids such as carbon dioxide (CO_2) overcomes many drawbacks linked to the use of liquid organic solvents such as liquid hexane. Solvents commonly used present problems of toxicity and residual content after extraction. In addition to toxicity, there is also the problem of security during storage due to flammability [1]. In this context, using supercritical CO_2 has many advantages: it is nontoxic, not flammable and CO_2 separation is easily done by a simple depressurization. There is no residual organic solvent trace in the final products. Besides, the extraction by supercritical CO_2 decreases the unit operation number in the process in comparison with classical processes. The CO_2 critical temperature is low (31 °C), which is interesting for the extraction of thermo-labile components. By varying pressure beyond its critical value (73.8 bar), it is possible to control the solvent power to a large extend, permitting an important selectivity. Eventually, supercritical CO_2 presents other interesting physical properties: low viscosity close to that of gases and high matter diffusivity, between liquids and gases ones. These tunable properties are very important for the local efficiency of extraction in a porous solid matrix. Typically in SCF extraction, a simple solvent gas, such as CO_2, is contacted with a solid or liquid phase at high pressure and moderate temperature. Slight changes in the temperature or pressure of the system can cause large changes in the density of the solvent and consequently in its ability to solubilize heavy nonvolatile waste compounds from the solid or liquid phase. For example, by manipulation of the system pressure, a nonvolatile can be extracted. Following a pressure letdown, generally to below the system's critical conditions, this same material can be completely precipitated from the solvent. Thus, the SCF phenomenon offers a unique opportunity for separation and recovery of difficult-to-separate materials in one processing stage. Supercritical fluid densities compare to liquid densities; however, their viscosities and diffusivities are intermediate to typical liquid and gas values of these properties. Thus, SCFs have the solvent power of liquids with better mass-transfer characteristics than typical liquids. Consequently, separation efficiencies for SCF extractions can be much higher than for liquid solvent extractions.

In other words, the diffusivity of supercritical CO_2 is one to two orders of magnitude higher than for other fluids, which permits rapid mass transfer, resulting in a larger extraction rate than that obtained by conventional liquid extraction [2]. Several studies about supercritical fluid extraction have been carried out in the last few decades. For example, Ge et al. [3] reported the use of supercritical CO_2 as well as CO_2 and ethanol mixture to extract andrographolide in an own built extractor unit. Kumoro et al. [4] investigated the effect of the solvent flow rate, pressure, and temperature on the supercritical CO_2 extraction of andrographolide. In addition, Chen et al. [5,6] investigated the influence of magnetic field on the morphology of the andrographolide from supercritical CO_2 extraction-crystallization and the recrystallization of andrographolide using the supercritical fluid anti-solvent process.

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The effectiveness of supercritical fluid extraction (SFE) from such matrices is difficult to predict due to the complex interplay of temperature, pressure, matrix type, and co-solvent type and amount. A systematic study of the rates of extraction of PAHs, or similar mixtures, from a highly contaminated topsoil or sediment has yet to appear [6-18]. Most of the studies have either been on model solid matrices (many with spiking), have focused on a single contaminant, or have looked only at total recoveries. In addition, in SFE of porous solids, solubility effects alone can sometimes explain the influences of temperature and density on recoveries [19].

Among the many related objectives of supercritical carbon dioxide extraction applications one can point out PAHs from environmental samples [20], SCE advantages over classical liquid solvent extraction [21], the SCE success and some of the future research needed to upscale SCE process [22], comparison of SCE method with other techniques [23], the use of selective SCE to study sorption/desorption processes and bioavailability of persistent organic pollutants (POPs) in sediments [24], etc.

Based on the above discussions, the efficiency of supercritical CO_2 extraction can be affected by many factors including pressure, temperature and extraction duration. So, in this paper we have investigated the effects of SCF temperature, pressure, static time, and flow rate on total recoveries of the contaminations from clay soils by one-factor-at-a-time design of experiments.

Finally, the content of the activated catalysts was analyzed by two different analyzing tests: GC and bromine index. Gas chromatography (GC) is used in analytical chemistry for separating and analyzing compounds that can be vaporized without decomposition. Typical uses include testing the purity of a particular substance, or separating the different components of a mixture (the relative amounts of such components can also be determined). In some situations, GC may help in identifying a compound. Gas chromatography-mass spectrometry (GC-MS) is a method that combines the features of gas-liquid chromatography and mass spectrometry to identify different substances within a test sample. Applications of GC-MS include drug detection, fire investigation, environmental analysis, explosives investigation, and identification of unknown samples. In this regard, the GC-MS analyses were used to identify the contents of the catalyst. In addition, bromine index was used to find if the activated catalyst was sufficiently activated.

In petrochemical enterprises, aromatic streams obtained from catalytic reforming and cracking processes always contain undesirable trace olefins [25] which are harmful to the downstream technological processes and the applications of aromatics [26]. Hence, the impurities must be removed before aromatic streams are routed to the petrochemical processes provided with the suitable treatment technologies [27]. Two processes have been proposed for removing trace olefins from aromatics: activated clay treating and catalytic hydrogenation treating [28]. Based on this fact, the bromine index of the processed hydrocarbon using activated catalyst was measured to find if the activated catalyst is efficient or not.

EXPERIMENTAL

1. Materials

Tonsil CO 610 G was kindly supplied from Jam Petrochemical Company. In addition, the CO_2 (purity>99.9%) was purchased from Abughadareh Gas Chemical Company, Iran. The particle size distribution, physiochemical properties and chemical analysis of used Tonsil CO 610 G are given in Tables 1-3. In a refinery, aromatic streams are obtained from catalytic reforming and thermal cracking, and these streams usually contain trace olefins such as monoolefins, multiolefins, and styrene. These olefins must be removed, for they may cause negative effects on the following operation. Clay treatment and catalytic hydrogenation treating utilizing Tonsil CO 610 have been widely used for removing trace olefins from aromatics. Clay treatment is simple to operate, while the particular clay used especially Tonsil CO 610 has a very limited lifetime. In general, the Tonsil CO 610 is contaminated by olefins which reduces their active sites, and if these adsorbed olefins are removed from the catalyst sites, catalyst can be reused.

Table 1. Particle size distribution of Tonsil CO610 G

>1.25 mm	0.2%
1.25-1.0 mm	5.0%
1.0-0.5 mm	68.0%
0.5-0.25 mm	24.3%
<0.25 mm	2.5%

Table 2. Physiochemical properties of Tonsil CO610 G

Loose bulk density	840 g/*l*
Free moisture (2 hr, 110 °C)	7.0%
Loss on ignition (2 hr, 1,000 °C)	10.0%
pH (10% suspension, filtered)	7.7
Free acidity	0.3 mg KOH/g
Total acidity	1.7 mg KOH/g
Chloride content	0.3 mg Cl/g
Surface area	100 m^2/g
0-80 nm	0.11 ml/g

Table 3. Chemical analysis of Tonsil CO610 G

SiO_2	62.0%
Al_2O_3	16.0%
Fe_2O_3	4.3%
CaO	3.0%
MgO	2.8%
Na_2O	0.3%
K_2O	1.6%
Loss on ignation	9.8%
Total	99.8%

Tonsil CO 610 catalysts are one of the most used catalysts for refining of edible oils (e.g., raps oil), fats, waxes and mineral oils (production of lubricants), reclamation (re-refining) of spent oil. In addition, Tonsil CO 610 G in particular is utilized in the aromatic clay treatment unit.

2. Extraction Setup

The used extraction pilot plant designed for maximum pressure and temperature of 400 bar and 373.15 K, respectively, is shown in Fig. 1. A similar apparatus was used previously by a co-author [29]. Carbon dioxide supplied from a gas cylinder was liquefied through

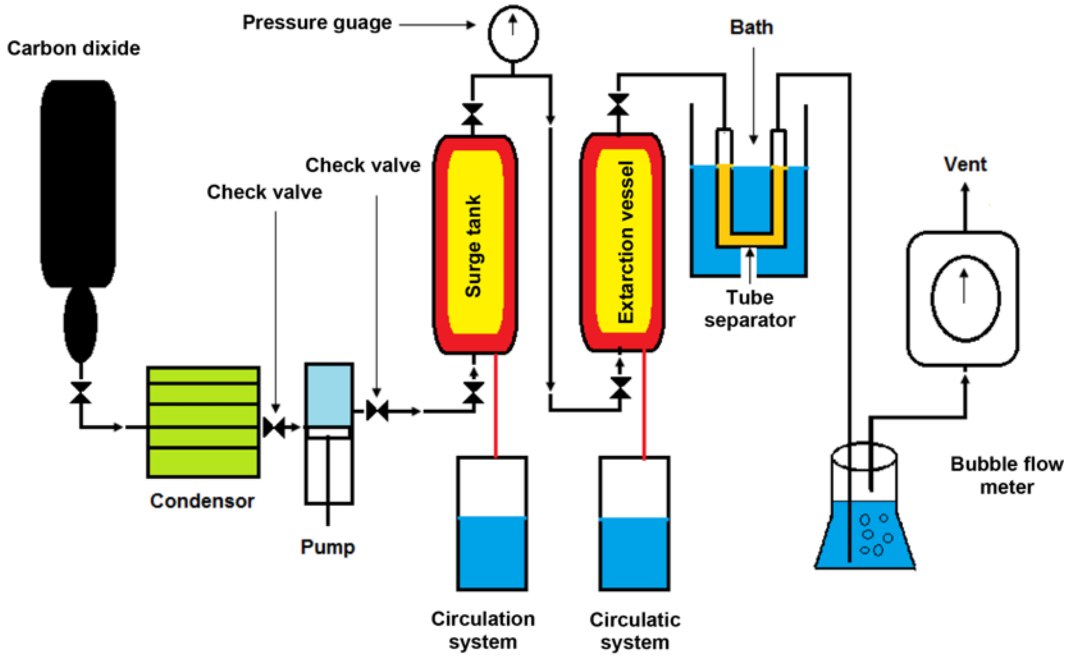

Fig. 1. Schematic diagram of the used extraction apparatus.

a cooling unit. Liquid carbon dioxide was compressed by a high-pressure air driven oil-free reciprocating pump (Haskel, USA), allowing flow into a surge vessel to dampen the fluctuations generated by the operation of the pump, and then went to a preheating coil and reached the supercritical condition. Also, at the outlet of the surge tank a bourdon gauge in the range of 0-400 bar by a division of 1 bar was placed to monitor the pressure of the system easily. Then supercritical carbon dioxide entered into the equilibrium cell (180 cc). The surge tank and the extraction vessel were surrounded by a regulated hot water jacket to set the temperature of system up to 373.15 K. The extraction temperature could be sensed easily by a PT-100 thermocouple with precision of 1 K. It must be mentioned that during the experiments, the extraction pressure and temperature were held constant in the range of 3% of instrumental full scale by continuous monitoring of the system operational conditions.

The contaminated soil (about 28 g) was packed by glass beads and glass wool in a stainless steel basket. The glass beads were used to increase the surface area between the contaminated soil particles and the SCF. Also, the glass wool was used to prevent carrying out the soil particles over the SCF flow. The basket was then placed into an extraction vessel and held in until the desired conditions had been obtained. In this procedure the difference between the initial and final weight of the basket is the amount of the extracted contaminations from the clay soil.

That is, after finishing the extraction process, we reweighted the sample and considered the difference between the initial and final

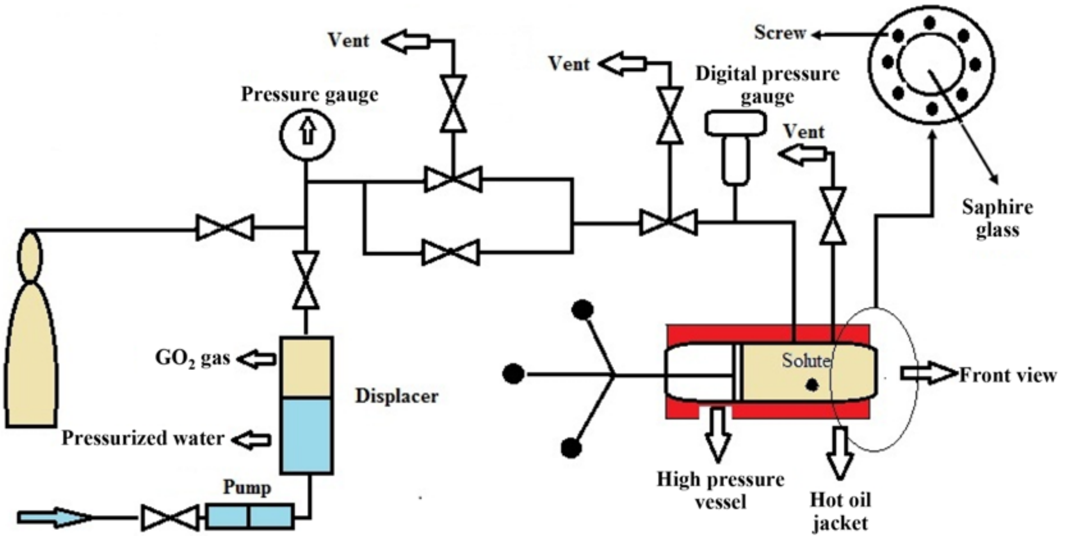

Fig. 2. The used apparatus for Bromine index determination.

mass of the soil as the amount of the extracted contamination. The mass of extracted contaminations was determined to be 0.1 mg by using a Sartorius BA110S Basic series balance. The typical mass of solute for each experiment was greater than 50 mg, giving a potential error due to weighing of 0.2 wt%. The vented carbon dioxide was passed through bubble flow meter with precise calibration of 0.001 ft^3. Also, the catalyst samples were dried before any measurements under a temperature of 323.15 K during a night to ensure no water or carbon dioxide was present in the samples.

3. GC-MS Analysis

GC-MS analysis was performed to reliably check the feasibility of the used method for the regeneration of the spent catalyst. In this direction, after filtering the sample, we used a GC-MS analysis instrument (Hewlett-Packard 6890) to check the composition of the poisoned catalyst and regeneration ones. The column used for separation was an HP-5MS separation column (25 m×0.25 mm i.d). The static phase was phenyl methyl cyclohexanol, which is a water absorber. The instrument temperature was changed from 333.15 K to 523.15 K with the rate of 3 K/min. The used gas was helium (purity>99.99%) at a constant injection rate of 1.2 cc/min.

4. Experimental Apparatus and Procedure for Bromine Index (BI) Determination

A PVT apparatus (see Fig. 2) was used to measure the Bromine index (BI) of the cleaned clays. The setup consisted of two main

Table 4. The obtained results of different experimental conditions[†]

Experiment no.	Flow rate (cc/min)	Static time (min)	Dynamic time (min)	Extraction temperature (K)	Extraction pressure (bar)	Initial weight of contaminated soil (g)	Final weight of contaminated soil (g)	Extracted contamination from soil (g)	Changed weight fraction %
Effect of flow rate									
1	42.6	85	10	313.15	100	27.7362	27.7173	0.0189	0.068
2	26.4	85	16	313.15	100	27.7173	27.67	0.0473	0.171
3	14.4	85	30	313.15	100	27.67	27.616	0.054	0.195
4	6.6	85	60	313.15	100	27.615	27.54	0.075	0.272
5	4.2	85	100	313.15	100	27.562	27.475	0.087	0.316
6	3.6	85	120	313.15	100	27.46	27.375	0.085	0.310
7	2.4	85	180	313.15	100	27.7362	27.6482	0.088	0.317
Effect of static time									
8	2.4	45	180	313.15	100	28.478	28.404	0.074	0.260
9	2.4	55	180	313.15	100	28.3832	28.2992	0.084	0.296
10	2.4	60	180	313.15	100	28.234	28.148	0.086	0.305
11	2.4	70	180	313.15	100	28.0265	27.9375	0.089	0.318
12	2.4	80	180	313.15	100	27.9355	27.8485	0.087	0.311
13	2.4	85	180	313.15	100	27.7362	27.6482	0.088	0.317
Effect of extraction pressure									
14	2.4	85	180	313.15	100	27.7362	27.6482	0.088	0.317
15	2.4	85	180	313.15	140	27.71	27.62	0.09	0.325
16	2.4	85	180	313.15	160	27.67	27.5795	0.0905	0.327
17	2.4	85	180	313.15	180	27.5565	27.4645	0.092	0.334
18	2.4	85	180	313.15	190	27.465	27.368	0.097	0.353
19	2.4	85	180	313.15	200	27.4432	27.3458	0.0974	0.355
20	2.4	85	180	313.15	210	27.3071	27.21	0.0971	0.356
21	2.4	85	180	313.15	220	27.1	27.0028	0.0972	0.359
22	2.4	85	180	313.15	250	27.1232	26.97	0.1532	0.565
23	2.4	85	180	313.15	280	27.256	27.07	0.186	0.682
24	2.4	85	180	313.15	310	27.3501	27.16	0.1901	0.695
25	2.4	85	180	313.15	330	27.01	26.82	0.19	0.703
Effect of extraction temperature									
26	2.4	85	180	308.15	200	28.6913	28.594	0.0973	0.339
27	2.4	85	180	313.15	200	27.4432	27.3458	0.0974	0.355
28	2.4	85	180	323.15	200	27.714	27.62	0.094	0.339
29	2.4	85	180	328.15	200	27.67	27.585	0.085	0.307
30	2.4	85	180	333.15	200	27.647	27.58	0.067	0.242
31	2.4	85	180	338.15	200	27.5542	27.49	0.0642	0.233

[†] All the experiments were performed at constant used volume of carbon dioxide (425 cc)

parts: (1) supplying supercritical CO_2, and (2) keeping equilibrium between solid and supercritical CO_2. CO_2 was first entered into the displacer and it was then pressurized by means of a reciprocating oil-free water-free high pressure manual pump (Haskel Pump, BURBANK, USA) to the desired pressure. The pressure in the displacer was monitored by a bourdon gauge pressure with a range of 0-450 bar (DEWIT) with the division of 1 bar. The homemade variable volume equilibrium cell was wrapped by a circulating oil jacket and heated to the desired temperature. The cell temperature was controlled by a feedback controller connected to the PT-100 thermocouple with precision of ±1 K. Also, the pressure of equilibrium cell was monitored by a digital pressure gauge (WIKA, 3769867) ranging up to 400 bar with the division of 0.1 bar. Similar to the extraction pilot plant, the temperature and pressure of the system were held constant in the range of 5% of the instrumental full scale by continuous monitoring of the operational conditions. The system pressure of each experiment was maintained to within ±0.1 bar of the desired pressure. The equilibrium cell was rated for pressures of 600 bar at 673.15 K. It was made of stainless steel 316 with an internal volume of 30 cc equipped with a sapphire window. All of the process tubing used in this apparatus was 1/8-inch O.D. tubing made of stainless steel 316.

Finally, 20 g of the clay soil was contacted with 20 g hydrocarbon in the PVT cell to determine the Bromine index for more reliable conclusion on the efficiency of the extraction process. In this direction, the mixed soil and hydrocarbon was kept under the pressure of 10 bar and temperature of 448.15 K for one hour.

RESULTS AND DISCUSSION

In the present investigation, 44 experiments (see Table 4-5) were conducted to investigate the effect of different parameters on the extraction of deactivatived components from contaminated clay soils. The used design of experiments was based on changing one factor at a time.

The list of targeted parameters which can affect SCE processes is itself impressive: characteristics of SCFs (with and without modifiers) and solid matrix, thermodynamic and kinetic conditions (e.g., temperature, pressure, density, and flow rate), water content, solute physical and chemical properties, etc. To select a unique set of optimum conditions under these circumstances for an efficient and cost-effective SCE process is a daunting task. To explain the application of SCF to the extraction of organics from soils, this paper is divided into different sections. In this study, the optimum conditions of dif-

Table 5. The obtained results from different extraction temperatures and pressures[†]

Experiment no.	Flow rate (cc/min)	Static time (min)	Dynamic time (min)	Extraction temperature (K)	Extraction pressure (bar)	Initial weight of contaminated soil (g)	Final weight of contaminated soil (g)	Extracted contamination from soil (g)	Changed weight fraction %
32	2.4	85	180	313.15	100	27.7362	27.6482	0.088	0.317
33	2.4	85	180	323.15	100	27.7165	27.6465	0.07	0.253
34	2.4	85	180	328.15	100	27.6465	27.5945	0.052	0.188
35	2.4	85	180	333.15	100	27.594	27.5535	0.0405	0.147
36	2.4	85	180	338.15	100	27.553	27.5135	0.0395	0.143
37	2.4	85	180	313.15	140	27.71	27.62	0.09	0.325
38	2.4	85	180	323.15	140	27.67	27.595	0.075	0.271
39	2.4	85	180	328.15	140	27.595	27.535	0.06	0.217
40	2.4	85	180	333.15	140	27.536	27.491	0.045	0.163
41	2.4	85	180	338.15	140	27.491	27.449	0.042	0.153
42	2.4	85	180	313.15	160	27.67	27.5795	0.0905	0.327
43	2.4	85	180	323.15	160	27.556	27.476	0.08	0.290
44	2.4	85	180	328.15	160	27.476	27.406	0.07	0.255
45	2.4	85	180	333.15	160	27.4	27.3487	0.0513	0.187
46	2.4	85	180	338.15	160	27.348	27.298	0.05	0.183
47	2.4	85	180	313.15	180	27.5565	27.4645	0.092	0.334
48	2.4	85	180	323.15	180	27.464	27.379	0.085	0.309
49	2.4	85	180	328.15	180	27.28	27.2029	0.0771	0.283
50	2.4	85	180	333.15	180	27.203	27.143	0.06	0.221
51	2.4	85	180	338.15	180	27.143	27.0849	0.0581	0.214
52	2.4	85	180	308.15	200	28.6913	28.594	0.0973	0.339
53	2.4	85	180	313.15	200	27.4432	27.3458	0.0974	0.355
54	2.4	85	180	323.15	200	27.714	27.62	0.094	0.339
55	2.4	85	180	328.15	200	27.67	27.585	0.085	0.307
56	2.4	85	180	333.15	200	27.647	27.58	0.067	0.242

[†] All the experiments were performed at constant used volume of carbon dioxide (425 cc)

[††] Results of runs 26-31 are used as runs 52-56

ferent parameters including flow rate, dynamic and static time and extraction pressure and temperature are obtained and the results of the performed experiments are explained in each section.

1. Optimization of Different Experimental Conditions

1-1. Effect of Flow Rate

SCF flow rate showed important effects on both solutes 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 analyte solubility and retention of analytes on matrix active sites (i.e., the solubility/elution process) or by the desorption/kinetic process [30].

Based on the above point, in the first part of this study, the effect of the flow rate was investigated on the extraction of deactivatived components from clay soils. To find the optimum flow rate, seven experiments with different flow rates (2.4, 3.6, 4.2, 6.6, 14.4, 26.4 and 42.6 cc/min) were performed while the other parameters including static time (85 min) and extraction temperature and pressure (313.15 K and 100 bar) were held constant. The obtained results show that the increase of the flow rate from 2.4 to 3.6 cc/min leads to an increase of deactivatived components amount, while further increase in the flow rate (3.6-42.6 cc/min) causes a reduction in the amount of extracted deactivatived components. This observed trend (see Table 4 and Fig. 3) could be related to this phenomenon that 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 are 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 desorption/kinetic step are efficiently extracted using either static or dynamic SCE. On the other hand, this observed trend could be described as follows: at the low flow rates (<4.2 cc/min) equilibrium can be achieved in the system, so the amount of extracted contaminations increases as the flow rate increases. But, when the flow rate exceeds a specific value, the gas velocity is higher than that enough to reach the equilibrium. Therefore, the amount of the extracted contamination will be decreased.

Finally, based on these experiments and the fact that there is no significant difference between extracted amount of contaminations of 2.4 and 4.2 cc/min flow rate, the 2.4 cc/min was selected as an optimum flow rate for the rest of the experiments.

1-2. Effect of the Static Time

In the second series of the experiments, six were performed to find the optimum static time to achieve the highest extraction amount of the soil contaminations. Static time is a duration during which the system is kept at desired operational conditions, namely, extraction pressure and temperature to ensure the equilibrium is reached in the system. In addition, the optimum static time is a duration in which the maximum amount of compound is solubilized in the supercritical carbon dioxide. In this part, six different static times (45, 55, 60, 70, 80 and 85 min) were tested while the other experimental conditions including extraction pressure and temperature (100 bar and 313.15 K), flow rate (2.4 cc/min) and dynamic time of 180 min were kept constant. As can be seen in Fig. 4 and Table 4, the amount of the extracted soil contaminations is increased as the extraction static time is increased. In other words, the obtained results reveal that a significant increase can be seen when the static time is increased from 45 min to 60 min.

But also, a slight increase is introduced as the static time is increased from 60 min to 85 min. This increase in the extracted amount of the soil contamination can be explained in this way: the static time is in a direct relationship to the saturation of the supercritical carbon dioxide with soil contaminations. So higher static time is necessary to achieve real saturation of the SCF with solute. Finally, the static time of 85 min was considered as an optimum static time for the rest of the experiments based on these findings.

1-3. Effects of Pressure and Temperature (Density)

Thermodynamic conditions of temperature and pressure (SCF

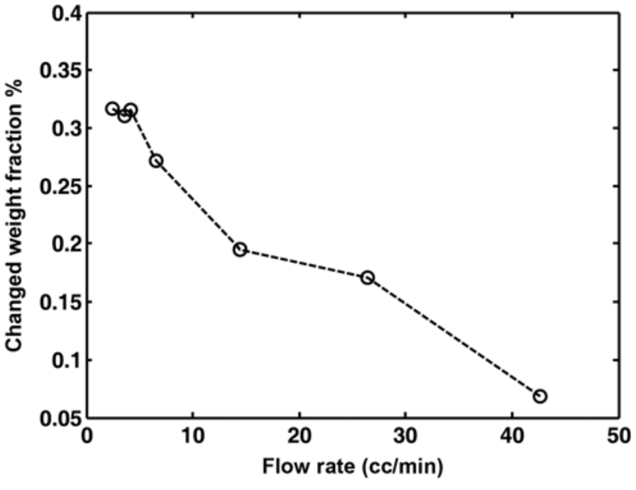

Fig. 3. The flow rate dependence of the amount of extracted contaminations.

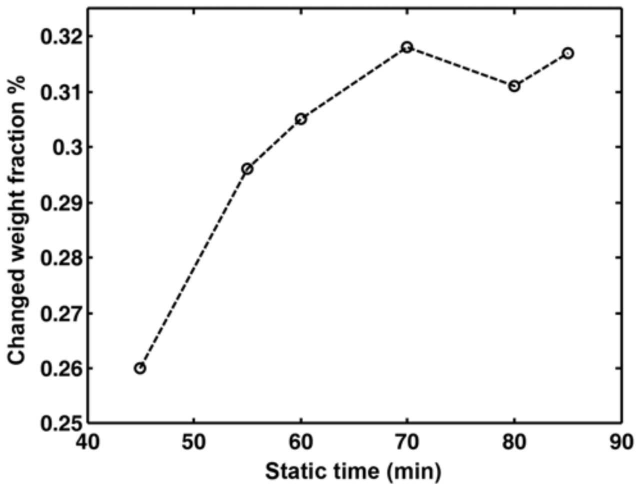

Fig. 4. The effect of static time on the amount of extraction of contamination from clay soil.

density) are the main factors affecting an SCE process. The experiments conducted in this section were divided into two parts, a) the optimum extraction temperature and pressure were obtained by changing one factor at a time, and b) five series of experiments were carried out to investigate the better interactions of the extraction temperatures and pressures.

In this regard, in the first stage of this section, the effect of pressure (100, 140, 160, 180, 190, 200, 210, 220, 250, 280, 310, 330 bar) at the fixed extraction temperature of 313.15 K was investigated. The obtained results revealed that the extraction efficiency of the supercritical carbon dioxide increases as the extraction pressure increases (Fig. 5(a)). Based on this obtained results it can be concluded that in the investigated pressure range, there is no optimum extraction pressure value.

In addition, in the last part of this study, the effects of the different thermodynamic parameters including extraction pressure (100, 140, 160, 180, 190, 200, 210 and 220 bar) and temperature (308.15, 313.15, 323.15, 328.15, 333.15, and 338.15 K) were investigated to clearly find the interaction between the extraction pressure and temperature on the extraction of contaminations from the deactivated clay soil. And, since working with high pressures and temperatures is difficult, the extraction pressure was increased just to 220 bar in the following experiments.

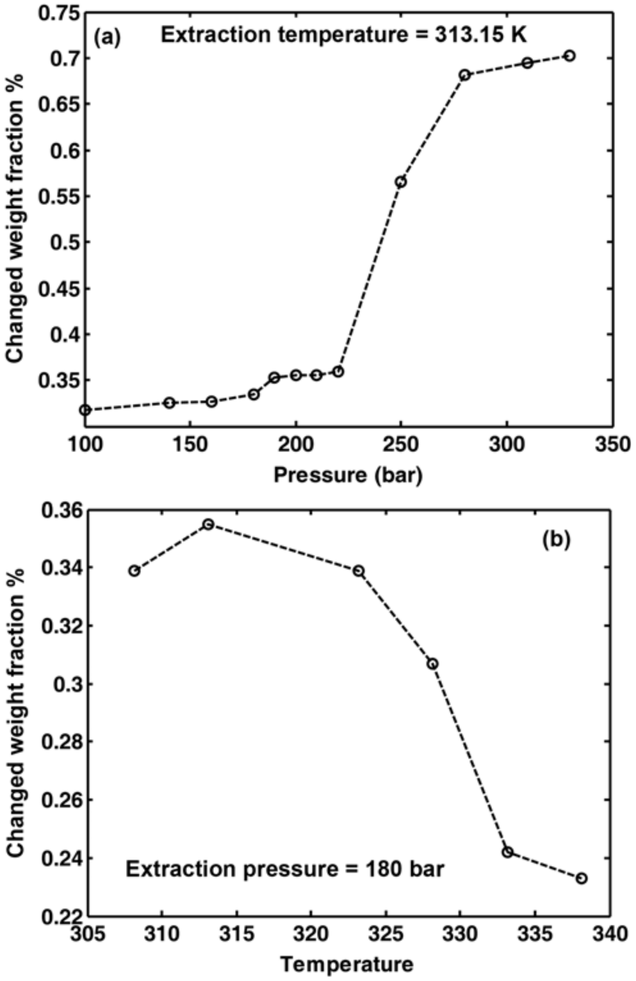

Fig. 5. (a) The effect of the different extraction pressures on the amount of extracted contaminations and (b) the effect of the different extraction temperatures on the amount of the extracted contaminations.

In the first series of experiments, eight were performed at different extraction pressures (100, 140, 160, 180, 190, 200, 210, and 220 bar) while the other experimental conditions (flow rate at 2.4 cc/min, dynamic time 180 min, static time at 85 min and extraction temperature at 313.15 K) were kept constant. The conducted experiments reveal that the increase of extraction pressure from 100 bar to 220 bar increases the amount of the extracted contaminations from 0.088 gr to 0.097. This obtained trend could be related to the density change of the supercritical carbon dioxide with the increase of extraction pressure. In other words, when the extraction pressure is increased, the density of the supercritical fluids will be increased, which causes higher solvating power of the supercritical fluids.

After examining the effect of extraction pressure, six experiments at different extraction temperatures (308.15, 313.15, 323.15, 328.15, 333.15, and 338.15 K) were conducted at the constant flow rate (2.4 cc/min), extraction pressure (200 bar) and static time (85 min). The obtained results are shown in Fig. 5(b) (see Table 4). By considering the obtained results, it is completely obvious that increase of the extraction temperature causes a reduction in the amount of the extracted contaminations.

This finding could be related to these phenomena that it is generally accepted that the temperature affects SCE recovery by changing both the thermodynamic (density) and kinetics of the process. There are opposite temperature effects on SCE such as decreasing uid density, and hence, the solute recovery on one hand and increasing solute solubility through its vapor pressure, on the other hand.

So, the obtained results show that in these experiments the dominant effect between the lower density (higher extraction temperature), which leads to lower solvating power and higher solubility through the vapor pressure of the solute, is the reduction of the solute solubility because of the lower supercritical density at the higher extraction temperatures. Besides its effect on solubility, temperature can affect rates of SFE through solute interactions with the matrix, as in kinetically-controlled desorption of contaminants [31]. Therefore, the total amount of solute that can be desorbed may sometimes depend on temperature alone and a higher temperature can increase recovery even at lower SCF density.

Finally, more experiments were carried out to better investigate the interactions of the extraction temperature and pressure. For this purpose, five series of different experiments were carried out. At each series, the extraction pressure was held constant while the extraction temperature (308.15, 313.15, 323.15, 328.15, 333.15, and 338.15 K) was varied. The obtained results shown in Fig. 6 reveal the before observed trends for all of the pressures and temperatures.

Many literatures reported successful results of different extraction conditions, some of which are discussed as follows. Screening studies of PCB desorption from soils/sediments were conducted in a laboratory scale SCE apparatus to provide basic information in this aspect [32,33]. The effects of temperature on PCB desorption were studied. The results showed the effectiveness of SCE as a technology for the cleanup of PCB contaminated soils/sediments at 30 min of extraction at 313.15 K 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

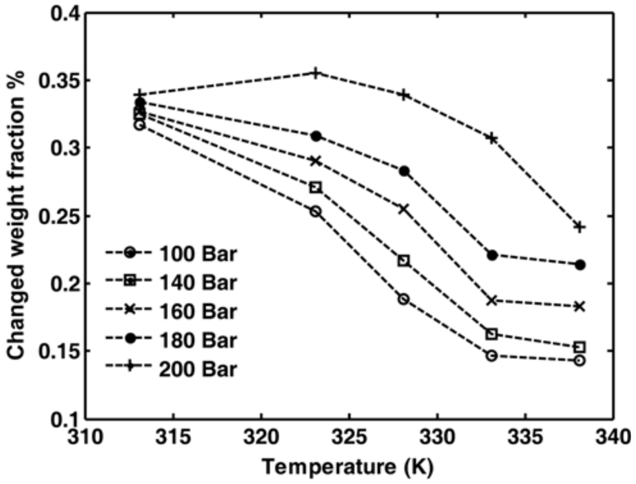

Fig. 6. Interaction of extraction pressure and temperature.

Table 6. The results of GC-MS analysis for different runs

Component %	Run			
	14	15	19	21
C1	----------	----------	----------	----------
C2	----------	----------	----------	----------
C3	----------	----------	----------	----------
C4	44.47^{P}	19.42^{P}	----------	1.73^{P}
C5	----------	----------	8.50^{P}	----------
C6	----------	----------	----------	----------
C7	----------	----------	----------	0.52^{A}
C8	----------	----------	----------	0.35^{A}
C9	----------	----------	----------	----------
C10	----------	----------	----------	----------
C10+	55.53^{P}	80.58	91.5	97.40

P: Paraffin, A: Aromatic, N: Naphthenic

recovery of SCE were studied [30]. SCE conditions using SC-CO_2 at 313.15-423.15 K were developed to allow sequential extraction of PCBs associated with rapidly desorbing, moderately, slowly, and very slowly desorbing sites on polluted sediments and soils [34]. 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 polychlorinated dibenzodioxins (PCDDs) and PAHs from different environmental samples were examined at constant fluid density and flow rate [35]. 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 SC-CO_2 at 405 bar or modified CO_2 at 80 and 473.15 K for 15 min of static followed by 15 min of dynamic SCE [36].

An increase in PAH recoveries was observed for all three samples by raising the temperature from 353.15 to 473.15 K, which demonstrated that the temperature enhancement was independent of the sample matrix. In addition, in extracting diuron and linuron from a soil, pressure increases improved recoveries to a greater extent at lower temperatures, due to the greater density changes possible there [11].

Moreover, 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 CO_2 at conventional (323.15 K) and high (473.15 K) temperatures [37]. At 323.15 K, 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 473.15 K. At 473.15 K, PCBs were effectively extracted at any pressure, while both higher temperature and pressure increased the recovery of PAHs from air particulates. These results showed that temperature is more important than pressure for achieving high extraction efficiencies when the interactions between pollutant and sample matrices are strong.

2. GC-MS Analysis of Thee Extracted Contaminations

In the previous sections, optimum conditions of different parameters including flow rate (0.04 cc/s), static time (85 min), extraction pressure (200 bar) and extraction temperature (313.15 K) were obtained. In the present section, some GC-MS analyses were conducted to investigate the composition of the extracted contaminations (see Table 6). The obtained analyses show that, at the lower extraction pressure (100 bar), more butane could be extracted while at the higher extraction pressures (200 and 220 bar) leads to extraction of heavier components (C10+). In addition, at moderate pressures (160 bar) a wide range of hydrocarbon component (C4-C8 and C10+) was extracted. Also, in all of the extraction pressures, extraction of heavier components (C10+) was observed and showed that using SCE technology could be advantageous to separate the heavy components from the contaminated soil. In addition, it is completely obvious that as the pressure increases, the power of supercritical carbon dioxide to extract more C10+ increases.

3. Determination of Bromine Index (BI Index)

Finally, several experiments were carried out to measure the Bromine index (BI index) of the regenerated and original spent catalysts. As previously described, 20 g of hydrocarbon (see Table 7) was contacted with 20 g of the clay catalyst (both spent one and regenerated one). Clay and hydrocarbon were contacted for total of 20 min to ensure enough residence time was given to the system. In addition, considering WHSV equal to 1, 20 min for contacting hydrocarbon and clay seems enough to ensure any reaction happens. Percolation tests were conducted seven times to find the 20 min

Table 7. Composition of the used hydrocarbon in BI index determination experiments

Component	Weight fraction %
Benzene	31.33
Toluene	53.99
C_8 paraffinic	0.02
C_8 naphthenic	0.03
Ethyl-benzene+styrene	0.28
P-xylene	2.89
M-xylene	6.39
O-xylene	2.68
C9 aromatic	2.39
C10 aromatic	0.1

Table 8. Results of the BI index for one of the performed experiment with and without acid washing

Test name	Unit	Regenerated with SCF without acid washing	Regenerated and acid washing	Spent catalyst	Input hydrocarbon
Bromine index	mgBr/100 g sample	11	9	25	110
Bromine number	gBr/100 g sample				
Mercaptans	ppm				
Water	ppm				
Carbonyl number	ppm				
Dissolved oxygen	ppb				
Peroxide number	ppm				
As	ppb				
Pb	ppb				
Hg	ppb				
Cu	ppb				

time for this BI determination experiment. Generally, two different experiments were conducted. In the first one, the BI index was measured immediately after percolation test (see Table 8) the second experiment was performed in this way that, after processing the clay with hydrocarbon, prior to BI index measurement; clay was acid washed and then the BI index was measured. The difference between these two different experiments is given in Table 8. Totally, the obtained results revealed that using acid washing can increase the efficiency of the clay regeneration if followed by supercritical extraction process. Acid washing is usually performed since the elimination of metals contaminating the clay soil is not possible by supercritical carbon dioxide extraction. The activated clay soil by supercritical carbon dioxide must be treated by acid to wash any undesirable metals from the catalyst surfaces to enhance the efficiency of the catalyst.

Finally, the GC-MS analysis can only be used to determine the composition of the extracted contaminations during the SFE operation. But, the BI index is an indication which reveals the amount of olefins (contaminations) that act as a poison for the clay catalyst. Generally, since the amount of olefins in the clay catalysts is significantly low, it is just the BI index can be used as an indication for the good performance of the clay catalyst. Totally, if the BI is below 10, the clay catalyst will efficiently remove the trace of olefin during the process, while the higher value of BI index means no proper olefin removal acts as a poison for following processes and catalysts. Considering all of these facts, if after SFE treatment the BI index is reduced to below 10; higher efficiency of regenerated catalyst is meant.

CONCLUSIONS

Forty different experiments were performed to find the optimum experimental conditions for different effective parameters including flow rate (2.4 cc/s-42.6 cc/min), static time (45-85 min), extraction pressures (100-330 bar) and temperatures (308.15-338.15 K) based on changing one factor at a time. The obtained results show that increase of the extraction pressure from 100 bar to 330 bar shows a significant increase in the amount of the extracted contaminations and a slight change in the extracted amount of the contamination were observed. In addition, the experiments reveal the dual effect of the flow rate. The experiments show that increase of the flow rate from 2.4 cc/s to 4.2 cc/min causes a slight change in the amount of the extracted contaminations. But, further increase in the flow rate from 4.2 to 42.6 cc/min causes of reduction in the extracted amount of the contaminations. Also, it was found that increase of the extraction temperature leads to decrease of the extracted amount of the contaminations. Finally, some experiments were performed that led to selection of 85 min as an optimum static time for the highest amount of extracted contaminations.

Furthermore, five GC-MS analyses were performed that show the success of the SCE technology to extract the heavy components (C_{10+}). Additionally, the analyses show that at the lower extraction pressures higher butane was extracted. While at the higher extraction pressures higher amount of heavy components was extracted. Finally, the obtained results demonstrated that SCE can be used to activate and clean the contaminated clay soil.

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