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جامعة الإمارات العربيـة المتحدة
United Arab Emirates University

United Arab Emirates University

College of Engineering

Department of Chemical and Petroleum Engineering

INVESTIGATION OF THE EFFECT OF SUPERCRITICAL CARBON DIOXIDE EXTRACTION ON THE ADSORPTION CAPACITY OF DATE PITS

Haliemeh Imad Sweidan

This thesis is submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering

Under the Supervision of Professor Ali H. Al-Marzouqi

November 2017

Declaration of Original Work

I, Haliemeh Imad Sweidan, the undersigned, a graduate student at the United Arab Emirates University (UAEU), and the author of this thesis entitled "*Investigation of the Effect of Supercritical Carbon Dioxide Extraction on the Adsorption Capacity of Date Pits*", hereby, solemnly declare that this thesis is my own original research work that has been done and prepared by me under the supervision of Professor Ali H. Al-Marzouqi, in the College of Engineering at UAEU. This work has not previously been presented or published, or formed the basis for the award of any academic degree, diploma or a similar title at this or any other university. Any materials borrowed from other sources (whether published or unpublished) and relied upon or included in my thesis have been properly cited and acknowledged in accordance with appropriate academic conventions. I further declare that there is no potential conflict of interest with respect to the research, data collection, authorship, presentation and/or publication of this thesis.

Student's Signature: ____________ Date: 29/4/2018

Approval of the Master Thesis

This Master Thesis is approved by the following Examining Committee Members:

1) Advisor (Committee Chair): Ali H. Al-Marzouqi
   Title: Professor of Chemical Engineering
   Department of Chemical and Petroleum Engineering
   College of Engineering
   Signature Ali Hassan Date 15/3/2018

2) Member: Basim Abu-Jdayil
   Title: Professor of Chemical Engineering
   Department of Chemical and Petroleum Engineering
   College of Engineering
   Signature ____________ Date 15\3\2018

3) Member (External Examiner): Ana Aguiar Ricardo
   Title: Professor of Chemical and Biochemical Engineering
   Department of Chemistry
   Institution: NOVA University of Lisbon, Portugal
   Signature ____________ Date 18\3\2018

This Master Thesis is accepted by:

Dean of the College of Engineering: Professor Sabah Alkass

Signature ______________________ Date 29/4/2018

Dean of the College of Graduate Studies: Professor Nagi T. Wakim

Signature ______________________ Date 1/5/2018

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Advisory Committee

1) Advisor: Ali H. Al-Marzouqi
Title: Professor of Chemical Engineering
Department of Chemical and Petroleum Engineering
College of Engineering

2) Co-advisor: Naeema I. Al Darmaki
Title: Assistant Professor of Chemical Engineering
Department of Chemical and Petroleum Engineering
College of Engineering

3) Member: Yaser E. Greish
Title: Associate Professor of Materials Chemistry
Department of Chemistry
College of Science

Abstract

This thesis aims to develop and investigate an innovative use of date pits, a common and abundant agricultural waste in the UAE. It is suggested that date pits may be used to produce date pit oil, and the powder residue from this extraction process may be used as a low cost adsorbent for removal of lead from water. This thesis aims to investigate the effects of the parameters pressure, temperature, and particle size on the extraction yield when using supercritical carbon dioxide (SC-CO_2) to extract oil from date pit powder. This oil is a valuable component which has many applications in pharmaceutics and foodstuff. The residue powder, symbolized by CO_2-DP, is then investigated as a possible adsorbent for removal of lead ions from water. The adsorption capability of CO_2-DP is then compared to that of raw date pits (R-DP) and the residue powder of Soxhlet extraction (S-DP). A Box-Behnken RSM design is used to optimize the adsorption parameters, namely adsorbent dose, lead concentration, and adsorbent type. The highest yield of date pit oil obtained from SC-CO_2 extraction, 10.29%, was achieved at pressure 500 bar, temperature 40℃, and particle size range <63 µm. The maximum extraction yield of SC-CO_2 is about the same as the extraction yield obtained from Soxhlet extraction, 10.3%, indicating that SC-CO_2 extraction is a reliable method for extracting oil from date pits. Furthermore, out of the three adsorbents tested, adsorbent type was not found to have a significant effect on the adsorption capacity for lead removal. At a constant pH of 4, the optimum adsorption conditions were found to be: dose of 0.0052 g/mL solution, lead concentration 196 ppm, time of 10 hours, and adsorbent type CO_2-DP. It is therefore suggested that oil be extracted from the date pits powder and the residue used in adsorption. In this way two useful products are produced from a readily available agricultural waste.

Keywords: Supercritical Fluid Extraction, Date Pits, Adsorption, Response Surface Methodology.

Title and Abstract (in Arabic)

تحري أثر عملية الاستخلاص باستخدام ثاني أكسيد الكربون في الحالة الفائقة على قدرة أنوية التمر على ادمصاص الرصاص

الملخص

تهدف هذه الرسالة إلى تحري وتطوير طريقة مبتكرة للاستفادة من نواة التمر، و هي أحد المخلفات الزراعية المنتشرة والمتوفرة بكثرة في دولة الإمارات العربية المتحدة. و يقترح استخدام نواة التمر في إنتاج زيت أنوية التمر و استخدام المسحوق المتبقي من عملية الاستخلاص كماز منخفض التكلفة في إزالة الرصاص من الماء. وتهدف هذه الرسالة إلى تحري أثر عوامل الضغط والحرارة وحجم الجزيئات في إنتاجية عملية الاستخراج عند استخدام ثاني أكسيد الكربون في الحالة الفائقة لاستخراج مسحوق أنوية التمر. يعتبر زيت نواة التمر مكوناً مهماً و لديه العديد من التطبيقات في المستحضرات الصيدلانية والمواد الغذائية. و قد تم البحث عن إمكانية استخدام بقية المسحوق، والمختصرة كـ CO_2-DP كماز يساهم في عملية إزالة أيونات الرصاص في المحلول. ثم تمت مقارنة قدرة المسحوق على استخلاص (R-DP) لقدرة نواة التمر و بقية المادة المترسبة من استخراج (S-DP). و قد تم استخدام Box-Behnken RSM design لتحديد حالة عوامل الاستخراج من جرعة الماز، ومن ضمنها قيمة تركيز الرصاص ونوع الماز. تقدر أعلى إنتاجية لزيت أنوية التمر باستخدام ثاني اكسيد الكربون في الحالة الفائقة بـ 9.9 و قد تم الحصول عليها عند ضغط 500 بار و درجة حرارة 40 سيليزي و حجم جزيئات أصغر من 63 ميكروميتر. وتعتبر أعلى انتاجية لعملية الاستخراج لثاني أكسيد الكربون في الحالة الفائقة هي 9.9 وهي تتقارب للغاية لانتاجية عملية الاستخراج من (S-DP) و هي بقيمة 10.3 مما يدل على أن استخدام ثاني أكسيد الكربون في الحالة الفائقة مناسب وفعال لاستخراج الزيت من أنوية التمر. و علاوة على ذلك، تمت دراسة ثلاثة مواد مازة أخرى، و تم الاستنتاج أن لدى ثاني أكسيد الكربون في الحالة الفائقة أعلى قدرة على إزالة الرصاص. و تمت الملاحظة بأن أفضل استخلاص عند مستوى رقم هيدروجيني 4 وكانت الشروط كالتالي: جرعة 0.0052 جرام/مل، تركيز الرصاص 196 جزء/مليون جزء، الزمن: 10 ساعات، و نوع الماز: ثاني أكسيد الكربون في الحالة الفائقة. و لذلك فمن المقترح استخراج الزيت من مسحوق أنوية التمر وأن يتم استخدام المادة المترسبة في الاستخلاص. و بهذه الطريقة، يتم انتاج مادتين مفيدتين من مخلف زراعي متوفر.

مفاهيم البحث الرئيسية: الاستخلاص باستخدام مميع في الحالة الفائقة، أنوية التمر، الاستخراج، منهجية سطح الاستجابة.

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Special thanks go to my parents and siblings who have not only supported me in my endeavors but made it possible for me to pursue them. Thank you all for being patient during all the late nights and all the time I spent away from you. I hope this thesis is as rewarding for you as it is for me.

Dedication

To my beloved parents and family for their constant patience and support

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List of Abbreviations

AC	Activated carbon
ANOVA	Analysis of variance
CO_2-DP	Date pits residue of supercritical carbon dioxide extraction
c_e	Equilibrium concentration, ppm
c_0	Initial concentration, ppm
DP	Date pits
ICP	Inductively coupled plasma
M	Mass, g
OFTAT	One factor at a time
P	Pressure, bar
q	Uptake, mg/g
q_e	Equilibrium uptake, mg/g
q_m	Maximum uptake, mg/g
R-DP	Raw date pits
RSM	Response surface methodology
SC-CO_2	Supercritical carbon dioxide
SCF	Supercritical fluid
S-DP	Date pit residue of solvent extraction
SEM	Scanning electron microscope
SFE	Supercritical fluid extraction
T	Temperature, ℃
V	Volume, mL

Chapter 1: Introduction

1.1 Overview

One of the most important challenges we are faced with in the modern world is how to use our limited resources to their fullest potential. One of the ways this can be done is by finding new uses for waste products, or by-products of common processes. One of the most abundant agricultural waste products in the UAE is date pits. Date pits are often the result of the manufacturing processes of date syrup, date paste, and other date products.

The oil extracted from date pits has been the subject of several studies, including Besbes, Blecker, Deroanne, Drira, and Attia (2004) who studied the lipid profile of Deglet Nour and Allig date pit oils. Their results showed that date pit oil may be used in culinary and pharmaceutical applications. In addition, they investigated the phenolic, tocopherol and sterol profiles (Besbes, Blecker, Deroanne, Bahloul, et al., 2004). Also the potential of date pit oil as a possible biodiesel source has been studied (Azeem et al., 2016; Jamil et al., 2016).

In addition to producing oil, date pits have also been investigated as possible adsorbents and precursor materials for production of activated carbon. They have been shown to be an effective adsorbent on their own and an appropriate precursor for activated carbon production. However, to the best of the author's knowledge, no previous study has used extracted date pits powder as an adsorbent.

Lead is a common pollutant produced from industries such as mining, smelting, printing, metal plating, and the production of batteries, paints, alloys, ceramic glass and plastics. Lead can infiltrate the water supply and is one of the most toxic pollutants to human health. It can cause damage to the kidneys, liver, brain, nervous system, and reproductive system in humans (Anantha & Kota, 2016). Lead removal from water sources is a serious and important environmental challenge. Lead removal may be achieved by many methods such as ion-exchange, and electrocoagulation but adsorption is one of the most widespread methods for lead removal (Anantha & Kota, 2016).

This thesis investigates the use of date pits, a common and abundant agricultural waste, to not only produce a valuable product, date pit oil; but to also solve an important environmental issue; water pollution. It is proposed that date pits could be utilized to produce oil through supercritical fluid extraction and the solid residue of this process can be used as an adsorbent for lead removal from aqueous solutions. This investigation opens the door to learn more about the application of supercritical fluid technology in extraction, and to find ways to utilize date pits in adsorption for water purification.

Chapter 1 will provide an overview of the problem, as well as all relevant literature. Chapter 2 will discuss the experimental methods used to achieve the thesis objectives. Chapters 3 includes a presentation of the obtained results and an in-depth discussion of the results. Chapter 4 includes a summary of the main conclusions drawn from the study and recommendations for future work.

1.2 Statement of the Problem

This thesis aims to address two main environmental problems: removal of lead ions from solution; and utilization of agricultural waste in a beneficial way. It is proposed that the process of extracting lipids from date pits can be used to produce date pit oil, and that the powder residue of this process can be used as an adsorbent. Date pit oil is a valuable product with a large potential in cosmetics, pharmaceutics, and even biofuel. Therefore, an efficient and convenient method for its recovery is needed.

To this end, an investigation of the use of supercritical fluid extraction will be conducted. Supercritical fluid extraction has proven to have advantages over traditional solvent extraction; particularly being better at extracting thermally sensitive materials, and easily separating the solvent from extract.

In addition, lead pollution is a serious environmental problem which needs to be addressed. When humans are exposed to lead serious health side effects can occur, including problems in the digestive track, nervous system, and reproductive system (Anantha & Kota, 2016). Therefore, finding low cost adsorbents with a high efficiency of lead removal is necessary. To that end, this thesis will compare the adsorption capacity for lead removal of three types of natural adsorbents: raw date pits (R-DP), the date pits residue from Supercritical Carbon Dioxide Extraction (CO_2-DP), and date pits residue from Soxhlet Extraction (S-DP).

1.3 Objectives

The main objectives of this study are to:

1. Investigate the effect of extraction parameters on the supercritical fluid extraction (SFE) of date pits.
2. Optimize the parameters for supercritical fluid extraction of date pits.
3. Investigate the effect of adsorption parameters.
4. Use Response Surface Methodology (RSM) to optimize the adsorption parameters.
5. Perform Soxhlet extraction and compare its yield to the yield obtained from supercritical fluid extraction.

6. Compare the adsorption capacities of raw date pits (R-DP), date pits residue from Soxhlet extraction (S-DP) and supercritical carbon dioxide extraction (CO_2-DP).

1.4 Relevant Literature

1.4.1 Production of Dates in the UAE

The date palm is one of the most important agricultural resources in the Middle East as a whole, and in the UAE in particular. The date palm can be found in many Middle Eastern countries including UAE, Saudi Arabia, Iran, Egypt, Iraq, Tunisia, Algeria, and many Mediterranean countries. The date fruit consists of a "fleshy pericarp and a seed which constitutes between 10 and 15 % of date fruit weight" (H. Liu et al., 2013). The annual world production of dates was 7.2 million tons in 2009 (Al-Farsi & Lee, 2011).

The UAE is one of the leading producers of date fruits in the world. The date palm recieves special care and attention not only as a valuable food source, but also as a heritage and cultural symbol. According to a 2010 FAO (Food and Agriculture Organization of the United Nations) report, the date palm population in UAE is about 40 million trees, 8.5 million of which are in Al Ain. The date palm occupies 15% of total cultivated land in the UAE. In 1996, 31,005 acres of date palm were harvested in the UAE. The annual production of dates reached 240,000 MT in 1995. In 1998, the UAE's 50,000 MT of exported dates was valued at $15 million (Food and Agriculture Association, 2010). According to the FOA, global date production in 2008 was 7.1 million tons and the UAE ranked fourth with a total production of 755,000 tons, about 11% of the global production. According to a 2011 study released by the UAE Ministry of Foreign Trade, domestic consumption of dates was

745,000 tons, 94% of which was domestically produced, with the remaining 6% imported (Emirates News Agency, 2011). Such a large population of date palms produces a large amount of agricultural waste which can be utilized in beneficial applications.

1.4.2 Uses of Date Pits

The date pit is one of the most abundant forms of agricultural waste in the UAE. Date pits are a by-product of several food-related industries including production of date paste, date confectionery, and date syrup (Al-Farsi & Lee, 2014). A large amount of date pit waste is produced from these activities, and its disposal can pose an environemntal poblem. However, more importantly, date pits contain many valuable components which can and should be utilized for many applications.

Commercially, ground date pits are used as animal feed, or as a supplement in animal feed. In fact research suggests that adding date pits to animal diets, achieves feed conversions comparable to or even better than diets which lack date pit powder (Hamada, Hashim, & Sharif, 2002).

In addition, research studies have been undertaken to evaluate and propose beneficial uses of date pits. Al-Farsi and Lee (2014) have proposed using date pits, which contain a higher amount of dietary fiber and antioxidents than date flesh, to enrich date paste. They found that the addition of crushed date pits to date paste increases the quality of date paste by increasing its firmness, antioxident content, dietary and fiber content, and the sensory quality of the date paste, as judged by consumer preferences. Hamada et al. (2002) have proposed using date pits as a food supplement due to their large amounts of fibre. Date pits may be properly milled and added to enhance food without negatively affecting the food’s sensory quality.

Furthermore, the carbohydrate content of date pits could be used for creating functional food components; which are components that can promote the health benefits of the food they are added to. These components include antioxidant, anti-microbial, or anticarcogenic ability. Another component of date pits, selenium, displays unique antioxidant properties (Hamada et al., 2002). In addition, a study conducted by Al-Farsi and Lee (2008) found that a significant amount of phenolic acids may be extracted from date pits by using a mixed solvent extraction process. At the optimum extraction conditions, a maximum of 193.83 mg phenolic acid/100 g date pits were extracted and purified. The significance of phenolic acids lies in their antioxidant, anti-carcinogenic, and antimicrobial properties (Al-Farsi & Lee, 2008). Hence, date pits have proven to be very useful in the fields of medicine and foodstuff.

This abundant agricultural waste provides an excellent resource due to its many valuable components. Coming up with uses for it would be beneficial in many applications. Since the majority of date pits nowadays are simply thrown away, more research and effort is needed to come up with beneficial uses of this agricultural waste and ways to commercialize these uses.

In addition to its value as a food item, date pits have also been investigated for use as an adsorbent material, and a precurser material to produce activated carbon, a common adsorbent. Further development of this field of study would allow the production of low cost adsorbents from an already readily available waste stream.

1.4.3 Composition of Date Pits

Like any natural material, date pits consist of many components, including fats, ash, protein, and carbohydrates. The approximate percentage of hemicellulose, lignin, and cellulose in typical date pits are 17.5, 11.0, and 42.5% dry weight, respectively (Al-Ghouti et al., 2010). Hossain, Waly, Singh, Sequeira, and Shafiur Rahman (2014) have summarized the major components of different varieties of date pits as shown in Table 1.

Table 1: Composition of date pits

Type of date seed	Moisture (g/100 g DP)	Fat (g/100 g DP)	Protein (g/100 g DP)	Ash (g/100 g DP)	Carbohydrate (g/100 g DP)
Khalas	7.5	10.5	5.7	1.05	78.3
Fardh	9.5	8.2	5.8	1.2	78
Lulu	10.9	10.5	5.2	0.91	74.7
DegletNour	11.2	10.1	5.6	1.1	83.1
Allig	10.3	12.5	5.2	1.1	81
Mabseeli	3.1	5	3.9	1	86.9
Um–sellah	4.4	5.9	5.4	1.2	83.1
Shahal	5.2	5.1	2.3	0.9	86.5
Barhe	10.6	7.5	5.7	1.06	75.1
Shikatalkahlas	9.6	7.4	5.3	0.97	76.7
Sokkery	12.1	6.5	6.4	0.96	74
Bomaan	9.6	6.4	5.4	1.02	77.6
Sagay	10.8	5.7	5.3	0.99	77.2
Shishi	10.4	6.2	5.7	0.94	76.8
Maghool	9.8	6.5	5.6	1.14	77
Sultana	10	6.6	5.2	0.91	77.2
Maktoomi	9.8	7.5	5.8	1.07	75.8
NaptitSaif	10.2	6.9	5.7	0.84	76.4
Jabri	9.9	7.1	5.4	0.96	76.7
Khodary	10.2	7.7	5.4	0.87	75.9
Dabbas	12.3	6.9	5.1	0.92	74.8
Raziz	12.5	8.8	6.9	0.99	70.9
Shabebe	11.5	7.7	4.8	1.09	75

1.4.4 Composition of Date Pit Oil

One of the most important components of date pits is its oil, which, as shown in Table 1 can range from about 5 – 12 % of the date seed composition. It can also be noticed that the Khalas variety of date seed, widely grown in UAE, is a variety, which has one of the highest content among other varieties. The oil of the date pit contains many valuable fatty acids. Table 2 lists a comparison of fatty acid profiles among different date pit types (Hossain et al., 2014). As shown in Table 2, the main components of most date pit oil are Myristic, Palmitic, Stearic, Oleic, and Linoleic Acids. Oleic acid is the major fatty acid, regardless of date seed variety (Hossain et al., 2014).

Table 2: Fatty acid composition (g/100 g fatty acids) of varieties of date pit oil

Type of date seed	Capric (C10:0)	Lauric (C12:0)	Myristic (C14:0)	Palmitic (C16:0)	Stearic (C18:0)	Palmitoleic (C16:1)	Oleic (C18:1)	Linoleic (C18:2)	Linolenic (C18:3)
Deglet Noor	0.8	17.8	9.84	10.9	5.67	0.11	41.3	12.2	1.68
Allig	0.07	5.81	3.12	15	3	1.52	47.7	21	0.81
Phoenix Canariensis	0.11	10.24	7.51	9.83	1.66	0.07	50	19.23	0.11
Khalas			13.72	12.52	3.48	0.13	55.1	8.88	0.09
Barhe			14.02	11.72	3.05	0.13	48.01	10.3	0.11
Lulu			14.72	11.41	2.8	0.13	45.6	9.45	0.05
Shikat Alkahlas			13.33	11.91	3.34	0.15	44.9	9.67	0.17
Sokkery			15.33	12.95	3.31	0.13	44.6	10.2	0.14
Bomaan			13.73	13.32	3.83	0.16	46.9	7.9	ND
Sagay			13.24	12.13	3.08	0.12	42.31	13.9	0.18
Shishi			14.23	12.92	3.42	0.13	46.2	10.7	0.21
Maghlool			14.73	12.01	3.52	0.13	47.3	11.5	0.04
Sultana			10.43	14.2	6.05	0.16	41.4	10.3	0.03
Fardh			13.54	12.12	3.88	0.16	48	9.06	0.04
Fardh and Khasab	0.35	38.81		15.09			36.51	9.21	
Maktoomi			12.73	11.31	2.7	0.15	44.4	10.05	0.03
NaptitSaif			14.7	12.41	3.15	0.15	51.4	11.7	0.17
Jabri			14.92	12.52	3.42	0.15	48.2	12.8	0.4
Khodary			17.92	13.34	2.78	1.14	50.3	8.33	0.1
Dabbas			18.23	12.41	2.87	0.15	48.1	9.02	0.14
Raziz			14.72	11.51	2.52	0.11	52.3	10.4	0.09
Shabebe			17.14	12.72	3.28	0.19	49.5	9.93	0.15
AlBarakawi		37.1		9.24	1.71		32.66	4.33	
Alqundeila		0.11		0.42	46.93				

1.4.5 Uses of Date Pit Oil

Date pit oil has proven to be one of the most valuable products that may be extracted from the date pit. Besbes et al. (2005) found that date pit oil may be used in culinary applications such as cooking or frying, since it can bear thermal treatments and has a good shelf life. Furthermore, the oxidative stability of date pit oil is higher than the oxidative stability of most vegetable oils. This is due to the fact that date pit oil contains a higher saturated fatty acid (SAFA) content than unsaturated fatty acid content (UFA). UFA makes oils more sensitive to oxidation. Date pit oil has a lower UFA content compared to other types of vegetable oil (Besbes, Blecker, Deroanne, Drira, et al., 2004). In addition to its use in food and culinary applications, date pit oil can be used in cosmetics, particularly in the production of UV protectors to protect against UV rays, which cause cellular damage (Besbes et al., 2005).

In addition, researchers have explored the use of date pit oil for fuel. Jamil et al. (2016) evaluated date pit oil as an alternative feedstock for biodiesel prodution and found it to have a satisfactory octane number 58.23, density 870 kg/m^3, cloud point of 4℃, pour point of -1℃, and kinematic viscosity of 3.97 mm^2/s (40℃). These properties suggest that date pit oil is a good source of lipids for the production of biofuels.

1.4.6 Extraction Methods

In order to recover valuable date pit oil from date pit powder, several extraction methods may be used.

The most widely used method is solvent extraction, which involves the addition of solvents to the date pit powder in order to dissolve desired components that are soluble in the solvent. A separation process is then undertaken to separate the solvent from the extract. Depending on which components are desired to be extracted, the solvent and extraction conditions are selected. Solvent extraction may involve the simple addition of solvents; or the use of the Soxhlet apparatus, which allows the constant repetition of several extraction cycles. Solvent extraction is one of the most suitable techniques for extracting oil from solid seeds, such as almond oil from almonds, and peanut oil from peanuts, or date pit oil from date pits.

As with all mass transfer operations, the effectiveness of extraction depends on factors such as the extent of the solubility of the extract in the solvent, often related to polarity; nonpolar solvents dissolve nonpolar extracts and polar solvents dissolve polar extracts. Also the concentration gradient between the solvent and the sample plays a role; the more unsaturated the solvent, the larger the eoncentration gradient, and the better its ability to absorb more extract. In addition, increasing the contact time and the contact area between the raw material and the solvent increases the mass transfer. The mass transfer area can be enhanced by increasing the surface area of the raw material, which can be done by using smaller particles.

Many previous research studies have relied on using solvent extraction with organic solvents, particularly petroleum ether and n-hexane. However less studies have attempted to use other methods such as supercritical fluids to extract date pit oil. Hence there is a need for further investigation into use of supercritical fluid extraction and its controlling parameters, which is one of the objectives of this research. The following sections elaborate more on widely used extraction methods.

1.4.6.1 Simple Solvent Extraction

Simple solvent extraction invloves adding a volume of the solvent (typically a liquid organic solvent) to the raw material and allowing for the mass transfer of the solute to occur from the raw material into the solvent. The main limitation of this method is that the raw material is exposed to the solvent only once and the solvent can become saturated, even when there is more solute to be extracted within the raw material. Hence not all the solute is extracted. However it is a useful method when the recovery of specific targeted components is desired. For example, in their attempt to recover phenolics, including phenolic acids and flavonoids. Al-Farsi and Lee (2008) added particular solvents to the date seeds in order to recover specific components. A solution of water and 50% acetone was used to recover phenolics from date pits. Furthermore, butanol and butane were added to the extract in the next step in order to purify it further by solvent fractionation. Hence, specific components can be targeted and recovered with simple solvent extraction by choosing the necessary solvents in the right proportions.

1.4.6.2 Soxhlet Extraction

Soxhlet extraction is a more complex form of solvent extraction which allows more efficient extraction by constantly exposing the solute to fresh solvent and allowing the cycle to repeat itself continuously.

Soxhlet extraction is an effective extraction method since the solvent is continuously boiling, evaporating, reaching the condenser, then condensing into the sample. The sample is always in contact with fresh, pure solvent, which increases the mass transfer. When pure solvent comes in contact with the sample, there is a larger concentration gradient, making the mass transfer more effective. In addition, repetition of the extraction cycle until no more extract is obtained, ensures that the entire extract has been extracted. Soxhlet extraction allows for complete recovery of the solvent, it is therefore economical.

Soxhlet extraction can be further enhanced with ultrasounds. Ultrasound-assisted Soxhlet extraction uses the conventional Soxhlet glasware, but ultrasound is applied to the Soxhlet chamber through an ultrasonic probe. This method has been shown to acheieve the same extraction yield as conventional Soxhlet extraction but with less extraction cycles (Luque de Castro & Priego-Capote, 2010).

The effieciency of the Soxhlet extraction process depends heavily on the solvent chosen to extract the solute. In addition to its solubility, solvents should also be chosen depending on their chemical stability, boiling point (the lower, the less energy will be consumed), price, and safety. Some desirable characteristics for a solvent include nontoxicity, noncorrosiveness, low viscosity, and the allowance of the formation of immiscable liquid states, which allows easier seperation of the extract and solvent (Luque de Castro & Priego-Capote, 2010). Selectivity can be enhanced by adding co-solvents to alter the solvent polarity.

Soxhlet extraction has been used by many researchers to extract date pit oil from date pits, as summarized in Table 3. Ali, Al-Hattab, and Al-Hydary (2015) performed an investigation to find out the parameters that would lead to most efficient extraction of date pit oil with Soxhlet extraction. They compared solvents methanol, 2-propanol, chloroform, n-hexane, and toluene for extraction of oil from date pits. The authors found that nonpolar solvents (chloroform, n-hexane, and toluene) produced a higher yield than polar solvents (methanol, 2-propanol). This was to be expected as lipids are nonpolar compounds and therefore dissolve much better in nonpolar solvents. Tuluene is the solvent which resulted in the highest yield since it has a higher boiling point than the other solvents, which allows more contact time between the solvent and the sample, which in turn enhances the mass transfer of oil from the date seeds to the solvent.

Though the extraction yield with Tuleune was higher, it was recommended that n-hexane be sued as the solvent for extraction. The solvent n-hexane has a lower boiling point, which means less energy has to be spent during extraction. In addition, tuleune is a heavy solvent and reaching its boiling point (111°C) requires time and energy. In addiiton, n-hexane is a more economic option than tuluene and its extraction yields are similar.

Furthermore, Ali et al. (2015) found that smaller particle size date pits produced higher yields of oil. The reason for this is that smaller particle size means larger surface area, which enhances the mass transfer of oil from the solid particle to the liquid solvent.

Hence, when considering the conditions needed for Soxhlet extraction of date pits, it is recommended to use petroleum ether or n-hexane, aim for a small particle size, and allow adequate time for the extraction cycle to repeat itself. The method followed by Besbes, Blecker, Deroanne, Drira, et al. (2004) was chosen for the purposes of this research, as it allows for adequate extraction. Yield (%) is calculated as shown in equation (1).

$$yield\ (\%) = \frac{mass\ of\ extract\ (g)}{original\ mass\ of\ sample\ (g)} \times 100\% \tag{1}$$

Table 3: Comparison of Soxhlet extraction of date pits

Reference	Date pit type	Solvent used	Yield (%)	Operating temp (℃)
Besbes, Blecker, Deroanne, Drira, et al. (2004)	Deglet Nour	Petroleum ether	10.19	40-60
	Allig		12.67	
Jamil et al. (2016)	Not specified	n-Hexane	16.5 (calculated by difference in weight rather than weight of oil)	70
Ali et al. (2015)	Zahidi (Iraq)	n-Hexane	8.5	

Despite its effectiveness, Soxhlet extraction does have some disadvantages. Soxhlet extraction is time consuming, difficult to automate, and organic solvents often have negative health and environmental impacts. In addition, a further seperation process is needed to separate the solvent from the extract (Luque de Castro & Priego-Capote, 2010).

1.4.6.3 Supercritical Fluid Extraction

In order to overcome the limitations and disadvantages of solvent extraction, supercritical fluids may also be used as solvents for extraction. Supercritical fluids (SCFs) are substances which exist beyond their critical temperature and pressure in a single state. In the supercritical state, the gas and liquid phases are no longer distinctive; the fluid can no longer be liquefied by increasing pressure, nor can gas be formed by increasing the temperature (Sihvonen, Järvenpää, Hietaniemi, & Huopalahti, 1999). Figure 1 shows different phases of a pure substance, including the supercritical fluid region.

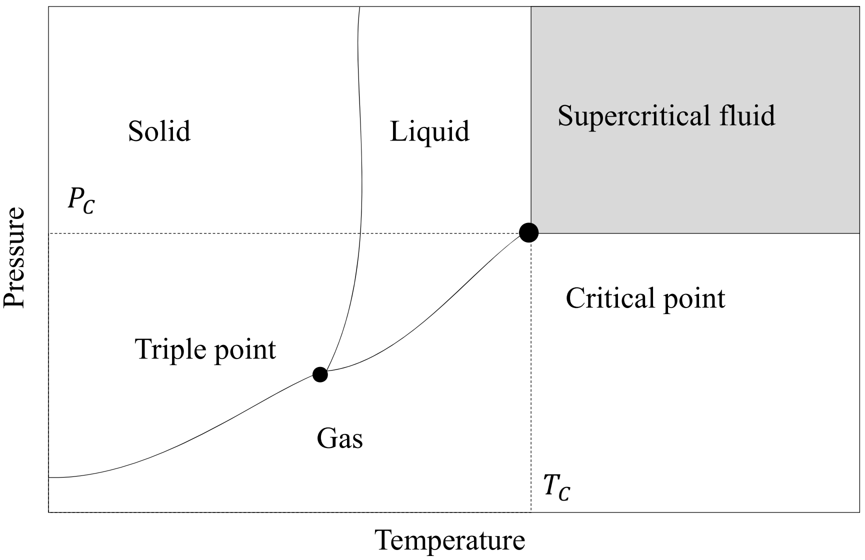

Figure 1: Phase diagram of a pure substance

Fluids in the supercritical state have properties which are intermediate between liquid and gas properties. For example, SCFs have diffusivities higher than pure liquids and viscosities higher than those for gases (Lee, 2005). This allows SCFs to be able to absorb and dissolve substances similar to liquids, and yet penetrate similar to gases. In the supercritical state, fluid properties such as density, diffusivity, and viscosity can be controlled simply by controlling the pressure or temperature. This distinct advantage is what allows supercritical fluids to be good solvents to use in the extraction process. By controlling the temperature and pressure, the user can manipulate the supercritical fluid's properties and achieve higher selectivity and products of higher purity. Supercritical fluids are superior solvents compared to liquid solvents, as the solvent strength can be controlled by controlling the density, which is easily controlled by adjusting the pressure. At the same time the gas like diffusivity allows for more favorable mass transfer (Sihvonen et al., 1999).

Supercritical fluids have other advantages over solvent extraction as well. Organic solvents may be expensive and their disposal causes an environmental challenge. Supercritical fluids, especially the inert ones such as CO_2 do not pose an environmental challenge, nor do they pose a health hazard to handlers. In addition, supercritical fluids have higher selectivity and may be used to produce components of higher purity – this is especially important for the food and pharmaceutical industries (Sihvonen et al., 1999). Also supercritical fluids do not require an additional separation process to separate the solvent from the extract. The supercritical fluid can simply be separated from the extract by releasing the pressure and allowing the fluid to go back to its gas state.

Much attention has been given to CO_2 for use as a supercritical fluid due to its many advantages. It is relatively easily to achieve the critical state of CO_2 as it has a low critical temperature of 31.3℃ and a low critical pressure of 73.6 bar. Moreover SC-CO_2 has a low viscosity of $3\text{-}7\text{x}10^{-5}$ Nsm^{-2} and no surface tension, which allows it to quickly penetrate various porous media. In addition, CO_2 is safe and convenient to use as it is nontoxic, non-flammable, inexpensive and readily available (Gao et al., 2010).

1.4.7 Parameters Affecting Supercritical Fluid Extraction

Supercritical fluid extraction is sensitive to parameters which influence the efficiency of the extraction. Among them are temperature, pressure, extraction time, (H. Liu et al., 2013), and particle size (Azzam, 2009). The following sections offer more elaboration.

1.4.7.1 Effect of Pressure

According to Sihvonen et al. (1999) even a small isothermal rise in pressure in the vicinity of the supercritical area results in a significant increase in fluid density, which increases its power as a solvent. It is exactly this property that allows the solvent strength of supercritical fluids to be much more easily controlled than the solvent strength of liquid solvents.

1.4.7.2 Effect of Temperature

The effect of temperature is not as straightforward as the pressure effect. On the one hand, increasing temperature (at constant pressure) decreases the density, which decreases the solvent power. However increasing the temperature also increases the volatility of the solute, thereby increasing its solubility in the solvent. These competing temperature effects are known as the crossover phenomenon (King et al., 1993; Taher, Al-Zuhair, Al-Marzouqi, & Hashim, 2011).

1.4.7.3 Effect of Particle Size

As particle size decreases, the surface area of the particle increases. Therefore it is expected that the mass transfer would be more enhanced as the mass transfer area is increased, resulting in a higher yield.

1.4.8 Supercritical Fluid Extraction of Date Pits

Unlike Soxhlet and simple solvent extraction, not many studies have been published regarding the use of supercritical fluids for the extraction of date pits. To the best of the author’s knowledge, only one study, by H. Liu et al. (2013) has been published on the topic of supercritical extraction of date pit oil. Therefore, one of the goals of this research project is to contribute to the very limited literature regarding the extraction of date pits with supercritical fluids.

The study published by (H. Liu et al., 2013) used orthogonal array method to optimize the extraction temperature, pressure, time, and number of extraction times when using supercritical carbon dioxide to extract phenolics from date pits. The total phenolic content (TPC) was used as the response variable. In order to extract the most phenolics from date pits, (H. Liu et al., 2013) found that the optimum extraction conditions were: temperature 50℃, pressure 350 bar, 2 repeated extractions for 2 hours each. At the optimum conditions 441.57 mg TPC per 100 g of date pit powder was extracted.

1.4.9 Environmental Problem: Lead Pollution

Lead pollution is one of the most pressing environmental issues of our time. In fact, lead is listed as the second most toxic substance in the list of prioritized hazardous substances issued by the US Agency for Toxic Substances and Disease Registry (ATSDR) (Samra, Jeragh, EL-Nokrashy, & El-Asmy, 2014). Lead is released into the environment as a result of the effluent wastewater from activities such as mining, smelting, printing, metal plating, and production of products such as batteries, paints, alloys, ceramic glass, plastics, and dyes (Anantha & Kota, 2016; Samra et al., 2014).

Since lead can infiltrate and contaminate the water supply, it contaminates every level of the food chain, from plants to humans (Anantha & Kota, 2016; Samra et al., 2014). Lead poison can be contracted by humans through polluted drinking water, or ingestion from food. It can also be contracted from the environment by inhalation of contaminated dust (Anantha & Kota, 2016).

The World Health Organization has set the limit for lead in drinking water to be 10 µg/L (0.01 ppm). Ingesting lead at levels higher than the body's tolerance can lead to health hazards including: physiological damage to the kidneys, liver, brain, nervous system, and reproductive system in humans (Anantha & Kota, 2016). Another hazard of lead poisoning in humans is its interference with heme synthesis, which leads to hematological damage (Samra et al., 2014). Chronic exposure to lead is associated with sterility, stillbirths, and neonatal deaths. Elevated levels of Pb (II) ions in the human body have been shown to cause a number of health issues including fatigue, a decrease reproductive ability, problems in the digestive track, and anemia. Lead poisoning is especially dangerous for children, as high levels of lead in the blood stream are associated with depression of brain development and cognitive skills (Anantha & Kota, 2016).

1.4.10 Current Options for Lead Removal

Heavy metals, including lead, do not naturally degrade (El-Naas, Al-Rub, Ashour, & Al Marzouqi, 2007). Hence, methods must be developed for their removal from wastewater to avoid health hazards and meet environmental regulations. Available methods include chemical precipitation, chemical oxidation and reduction, ion exchange, filtration, membrane processes, electrochemical treatment and evaporative recovery (Anantha & Kota, 2016; El-Naas et al., 2007). In addition, the parametric pumping with variation of pH (Stöhr, Bartosch, Kiefer, & Höll, 2001), as well as filtration using reverse osmosis, nanofilteration, and ultrafilteration enhanced with complexation (Neyens, Juliastuti, & Hulpiau, 2001) .

However, removal of lead by adsorption onto activated carbon remains the most effective and widely used method (Anantha & Kota, 2016). Many research projects have focused on the development of activated carbon from natural and low cost materials. This includes the use of the raw natural materials as adsorbents themselves, as well as subjecting them to various chemical activation processes.

1.4.11 Lead Removal by Adsorption

Adsorption is a process in which the adsorbing material is able to adsorb the solute to its surface. This process is sensitive to several parameters including solution pH; ratio of mass of adsorbent to solution; (called adsorbent dose); particle size of the solute; and contact time between the adsorbent and solution (Al-Ghouti et al., 2010; El-Naas, Al-Zuhair, & Alhaija, 2010)

Many attempts have been made to model the adsorption process. Adsorption isotherms model the relationship between the uptake, q (mg solute/g adsorbent) versus the equilibrium concentration, c_e, which is the concentration of the solute left in the solution once the adsorbent has become completely saturated. These measurements are taken for different solution concentrations at constant temperature and after the system has reached equilibrium.

Langmuir isotherm, displayed in equation (2), is based on the assumption of uniform and constant binding of the sorbate on the surface of the adsorbent (El-Naas et al., 2010). In the equation above, q_e refers to the uptake calculated based on the equilibrium concentration, c_e. The terms q_m and b are constants that refer to the maximum adsorption capacity, and the energy constant related to the heat of adsorption respectively.

$$q_e = \frac{q_m b c_e}{1 + b c_e} \tag{2}$$

Fruendlich Isotherm, equation (3), is a widely used isotherm in correlating equilibrium data. In equation (3) K_F and n are the Freundlich isotherm constants, which represent the adsorption capacity and the adsorption intensity, respectively (Samra et al., 2014). Unlike Langmuir isotherm, Fruendlich Isotherm does not have a thermodynamic basis and does not offer much physical interpretation of the adsorption data. This model does not have a maximum uptake and it does not approach Henry's Law at low concentrations (El-Naas et al., 2007).

$$q_e = K_F c_e^{1/n} \tag{3}$$

Sips isotherm, equation (4), combines Fruendlich and Langmuir isotherms. In equation (4), where K_{LF}, n_{LF} and a_{LF} are fitting parameters which do not have significant physical meanings (Al-Muhtaseb, El-Naas, & Abdallah, 2008). It approaches Langmuir isotherm at high concentrations and Fruendlich isotherm at low concentrations (El-Naas et al., 2007).

$$q_e = \frac{K_{LF} c_e^{n_{LF}}}{1 + (a_{LF} c_e)^{n_{LF}}} \tag{4}$$

1.4.12 Types of Adsorbents

Activated carbon is a well known and commonly used adsorbent for a wide variety of adsorbates, including organic and inorganic materials. It is particularly effective due to its large surface area and chemical properties, including the polarity and nature of the functional groups on its surface. In addition, activated carbon is a highly porous structure, containing networks of interconnected macropores, mesopores, and micropores. Thus, it is expected that Various mechanisms are suspected to be the driving force behind adsorption, including and forces, such as ion exchange, covalent bonding, van der Waals forces, H-binding, dipole-dipole interactions, and cation- and water-bridging, are all mechanism for the adsorption of sorbates on activated carbon (Allaboun & Abu Al-Rub, 2016).

However, the production and regeneration of activated carbon remains an expensive undertaking. Therefore, many research projects have focused on the development of activated carbon from natural low cost or waste materials, particularly agricultural wastes.

Natural materials which have been used for lead removal from water include: Chlorella vulgaris (El-Naas et al., 2007), chicken feathers reinforced with chitosan (Anantha & Kota, 2016), cow bone (Cechinel, Ulson de Souza, & Ulson de Souza, 2014), leather (Yan, Luo, Lin, & Yang, 2017), coconut shell (Sekar, Sakthi, & Rengaraj, 2004), peach and apricot stones (Rashed, 2006), Alocacée shell, Mimosaceae husk, and Burseraceae sawdust (Eba, Biboutou, Nlo, Bibalou, & Oyo, 2011).

Raw date pits have also been used for lead removal. A study conducted by Samra et al. (2014) used waste date pits from the factories of Mansoura, Egypt. The date pits were dried and crushed to the particle size of 25-63 μm and added in controlled doses to aqueous lead solutions.

Furthermore, date pits have been used as a precursor material for the preparation of low cost activated carbon for the removal of several types of solutes. Generally, activated carbon derived from agricultural sources may be activated physically or chemically. Physical activation involves carbonization at temperatures below 700°C followed by gasification by oxidizing gases, such as steam, carbon dioxide, and oxygen at high temperatures, up to 1100°C. Chemical activation involves the addition of a chemical to the precursor material that restricts the formation of tars; commonly used chemicals include nitric acid, phosphoric acid, and hydrogen peroxide. The precursor is then carbonized and washed to produce the final activated carbon. After the heat treatment, the chemical is removed by washing (Allaboun & Abu Al-Rub, 2016).

Activated carbons have been prepared from waste date pits through various methods. Awwad, El-Zahhar, Fouda, and Ibrahium (2013) physically activated date pits by heating the date pits up to 700-800°C and introducing steam and N_2 concurrently. In addition they chemically activated the date pits by introducing 10% (w/v) calcium acetate at 700°C after passing through N_2. Danish, Hashim, Ibrahim, and Sulaiman (2014) prepared activated carbon from date pits with H_3PO_4 and N_2 gas. Various other studies have investigated methods for preparing activated carbons from date pits for the removal of various solutes, including methyl blue, lead, copper, rhodamin B, cadmium, and COD (Abdulkarim & Al-Rub, 2004; Bouhamed, Elouear, & Bouzid, 2012; Danish et al., 2017; El-Hendawy, 2009; El-Naas et al., 2010).

However, to the best of the author's knowledge, no study has investigated the residue date pit powder left after an extraction process as an adsorbent. Therefore, the objective of this project is not only to produce date pit oil, but also a low cost adsorbent material from the residue of the extraction process. The powder residue of both supercritical fluid extraction and Soxhlet extraction are investigated as adsorbents for lead removal from aqueous solutions.

Chapter 2: Materials and Methods

It is the objective of this project to produce not only date pit oil, but also a low cost adsorbent material from the supercritical fluid extraction of date pits. The powder residue left after the extraction process (both supercritical fluid extraction and Soxhlet extraction) is to be investigated as an adsorbent for lead removal from aqueous solutions. To the best of the author's knowledge, this is the first study to examine date pit residue powder as an adsorbent for lead removal.

2.1 Materials

About 4 kg of Khalas date pits were collected from Al Foah Date Factory, Al Saad, Al Ain, UAE. The Khalas date pit was chosen for the purposes of this experiment because of its high oil content, compared to other varieties of date pits, and because Khalas dates are readily available and widely grown in the UAE. The date pits were then soaked in distilled water and washed carefully to remove any remaining fruit. After washing, the date pits were dried in an oven at 60℃ for 7 days. They were then sent to be crushed by a heavy duty mill (Teeba Engineering Industries, power of 15.5 kW). The crushed date pits were then sieved using stainless steel sieves (Glenammer Engineering, UK). Lead nitrate $Pb(NO_3)_2$ (>99% purity) was purchased from Fisher Scientific. Diluted nitric acid (HNO_3) or diluted sodium hydroxide NaOH was used for pH adjustments.

2.2 Methods

2.2.1 Extraction Methods

2.2.1.1 Soxhlet Extraction

Soxhlet extraction was carried out in a fully automated Soxhlet extraction unit (model 2050 Soxtec, Avani). The machine was equipped with 6 Soxhlet posts. Date pits were placed in a thimble and completely immersed in solvent. The autoextractor was connected to an auto control unit in which the extraction program could be set. The auto control unit allowed for setting the immersion time (time the sample spends soaking in the solvent), washing time (the time spent repeating the extraction cycle), recovery time (the time spent recovering the solvent) and drying time (the time spent drying the sample of any remaining solvent). The oil produced from the autoextraction unit was separated from the solvent.

Petroleum ether 40-60 was chosen based on its ability to dissolve lipids, its low boiling point, its availability, and the safety of its use. Furthermore, Besbes, Blecker, Deroanne, Drira, et al. (2004) were able to obtain a high yield from this solvent. The Soxhlet extraction method used is based on the one reported by Besbes, Blecker, Deroanne, Drira, et al. (2004). The operating temperature was set at 140℃. The thimble was allowed to immerse in the solvent for 30 minutes. The sample then underwent 60 minutes of reflux washing, 10 minutes for solvent recovery, and 5 minutes of drying.

Soxhlet extraction with petroleum ether 40-60 in the fully automated Soxtec machine was carried out in duplicate. Crushed date pits (5 g, <63 µm) were added to a cellulose extraction thimble which was added to the machine’s Soxhlet post and the program was run. At the end of the process, the oil was collected and the yield was calculated as mentioned in equation (1) in section 1.4.6.2.

2.2.1.2 SC-CO_2 Extraction

SCF extraction was carried using ISCO SFX 200 supercritical fluid extractor, with supercritical carbon dioxide (SC-CO_2) as the chosen supercritical fluid, since it is relatively easy to reach the CO_2 critical point (31℃, 73 bar) and CO_2 is nontoxic to humans, inexpensive, chemically inert, non-flammable, and readily available (DeSimone & Tumas, 2003).

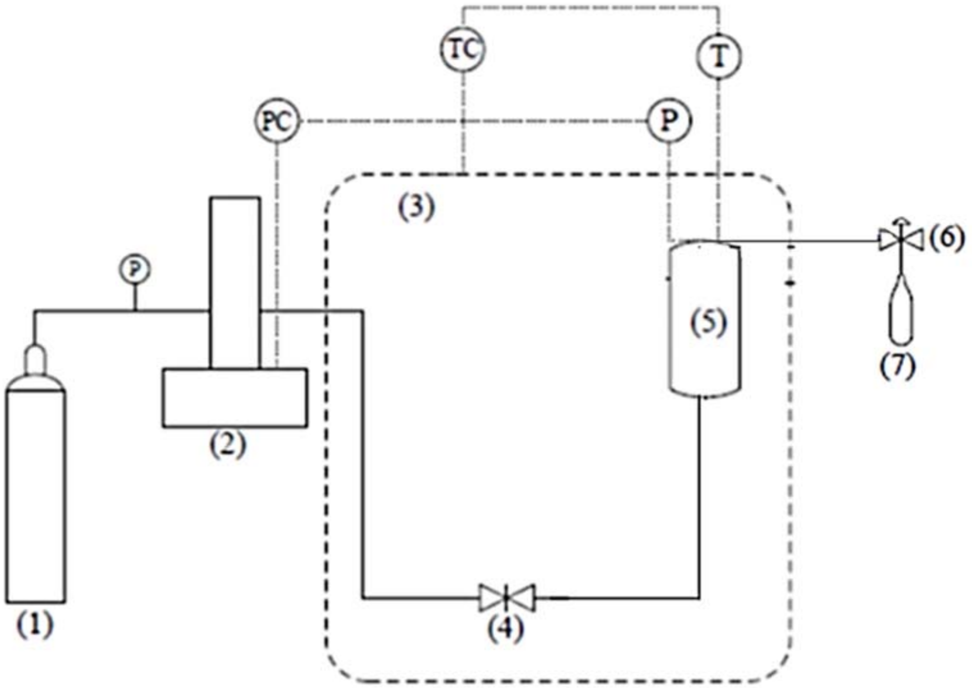

Figure 2: Schematic diagram of SCF Extraction set-up

As shown in the schematic diagram in Figure 2, this extractor is equipped with CO_2 cylinder with dip tube (1), pump controller (2), temperature controller (3), pre-extraction valve (4), extraction cell (5), micro-metering valve (6), extract collection vial (7). The maximum operating temperature, pressure and flow rate of the apparatus were 150℃, 516 bar and 107 mL/min, respectively. The temperature and pressure of the system were controlled by the controller, and the flow rate was controlled manually with a micro-metering valve (HIP 15-12AF1-V). To supply enough CO_2 to the syringe pump, circulating water bath (Polystat, Cole-Parmer Instrument Company, Chicago) connected to a heating coil surrounding the CO_2 cylinder was used. In addition, the outlet valve (6) was heated by a heating tape (Cole Parmer, US) which was wrapped around the valve. The heating tape was connected to a PID controller (Autonics, model TZN4S) which was fed by a thermocouple and controlled the valve temperature to 50℃. This temperature was hot enough to allow the oil to flow in the tubing, but not hot enough to destroy any volatile components the oil may contain.

During the process of supercritical fluid extraction of date pits, 3 grams of raw date pits (R-DP) were placed into the extraction cell (which had a capacity of 10 mL) where it was exposed to SC-CO_2 at previously determined temperature and pressure. The desired temperature and pressure were controlled by the controller. The syringe pump was used to bring the CO_2 up to the desired pressure, and the temperature controller maintained the incubator temperature at the set point.

Once brought to supercritical conditions, the SC-CO_2 at the set temperature and pressure was allowed to equilibrate with the sample in the extraction cell for 15 minutes. After the equilibrium time, the dynamic extraction part began. The extraction could be limited by time, or by volume of SC-CO_2. For the purposes of this study, the flow rate was kept at 4 mL/min by manually controlling the valve and 300 mL of CO_2 was allowed to pass. Upon exiting the valve (6), the oil was collected into the collection vile, meanwhile the solvent, SC-CO_2, was immediately separated from the extract upon the release of pressure by returning to its gas form. The collected oil was measured and the yield was calculated as mentioned in equation (1) of section 1.4.6.2.

In between each run, the extraction cell was removed and the pipes were flushed with 15-20 mL of n-hexane with the aim of removing any oil left in the pipes.

2.2.2 Adsorption Experiments

After exposing date pits to Soxhlet extraction and supercritical fluid extraction, the remaining residues (S-DP and CO_2-DP respectively) and raw date pits (R-DP) were used as adsorbents to remove lead from water. Factors that affect adsorption include pH, contact time, lead concentration, and adsorbent mass to solution ratio (called adsorbent dose). Therefore, screening experiments were conducted in order to determine the effect of the most important factors that would later be used to prepare a Response Surface Methodology (RSM) design.

Two screening experiments were conducted for the determination of the effect of pH and adsorbent dose. During all screening experiments, R-DP was used as the adsorbent with a particle size of <63 μm, and it was not subject to further drying than the procedure outline in section 2.2.1, the lead concentration was kept at 10 ppm, and the contact time was 24 hours. For the screening experiment for pH, the lead solutions varied in pH from 0-6. During the adsorbent dose screening experiment, the adsorbent dose was varied from 0.002-0.04 g/mL.

Lead solutions were prepared by dissolving lead nitrate $Pb(NO_3)_2$ was dissolved in ultrapure water to the desired concentration. The pH was then adjusted by adding diluted nitric acid (HNO_3) until the desired pH is reached. The pH meter used (Thermo Scientific Orion 3 Star) was calibrated with pH buffer solutions (Thermo Orion). All weight measurements were made with Sartorius analytic balance.

Following the screening experiments, batch adsorption experiments were carried out according to the conditions generated by the RSM, detailed in section 2.2.3.2. All adsorbents were dried in an oven at 120℃ for 24 hours, based on an initial TGA analysis which confirmed that the water content of the date pits is removed at 100-150℃. The appropriate mass of adsorbent was added to a 50 mL glass bottle. Then 25 mL of lead solution at the appropriate concentration and pH was added to the adsorbent. Contact time started as soon as Pb solution was added. The samples were then kept in a water bath shaker (Daihan Scientific, MaXturdy 18) where the temperature was set to 25℃ and the rotation speed to 150 rpm. After the desired time had passed, the samples were removed from the shaker. The adsorbent was separated from the solution by forcing the solution through a 0.45 µm syringe filter. The remaining lead solution and a sample of the initial lead solution were then taken for analysis.

Throughout the screening experiments, ICP was used to analyze the lead concentration. The calibration curve for the ICP was prepared by diluting 1000 Pb concentration standard solution (Chem-Lab NV, Belgium) to 1, 10, 20, and 30 ppm standard solutions with ultrapure water. When needed, the samples were diluted in ultrapure water to remain in the region of the calibration curve. The resulting concentration was then later multiplied by the dilution factor to get a reading for the concentration. For the series of RSM experiments, an ion selective electrode sensitive to lead was used (Hanna Instruments model 4112). This instrument was calibrated with 0.1 M lead standard solution (Hanna Instruments). During the RSM adsorption experiments, all lead measurements were taken with an ion selective electrode (ISE) (Hanna Instruments, USA).

For the adsorption isotherms, batches of adsorption experiments were carried out with CO_2-DP, the adsorbent with the highest capacity. A dose of 0.008 g/mL solution was added to each sample and kept for 24 hours with a shaking rate of 150 rpm, and a temperature of 25℃. The solution concentrations used were 5, 25, 90, 140 Pb concentration. After 24 hours the final lead concentration was measured and taken to be the equilibrium concentrations.

After obtaining the final and initial lead concentrations, the amount of lead adsorbed per amount of adsorbent, q (mg/g) was calculated using equation (5), where q is amount of lead adsorbed per amount of adsorbent (mg/g), c_0 is the initial lead concentration (mg/L), c_f is the final lead concentration (mg/L), V is the volume of solution used (L), and M is the mass of adsorbent used (g).

$$q = \frac{(c_0 - c_f)V}{M} \tag{5}$$

2.2.3 Experimental Design

2.2.3.1 Factorial Design for SC-CO_2 Extraction

In order to find the significance of the effect of extraction parameters on the yield of SC-CO_2 extraction of date seed oil, and to find the optimum conditions of supercritical fluid extraction, a 2^3 factorial experimental design, where 3 is the number of factors and 2 is the number of levels, was used. The purpose of this design was to evaluate the significance of the effects of pressure, temperature, particle size, and their interactions on the extraction yield. In addition, the factorial design can establish the statistical relationship between the extraction yield and the factors. It can also give the optimum conditions of yield. However, the underlying assumption of the General Linear Model is that there is a linear relationship among the yield and the factors. It is expected that pressure will be the most significant parameter. In order to confirm linearity and the adequacy of the model, test points in the middle of the two levels were tested.

In order to prepare the 2^3 factorial design, Minitab was used. Pressure and temperature were input as continuous factors, as they are continuous numbers and can take on any value. Meanwhile particle size range was a categorical factor, as particle sizes can only be obtained in ranges between sieve sizes. The two ranges used here were 63-125 μm, and <63 μm. Table 4 summarized the high and low values for the factor levels.

Table 4: Factors and levels for factorial design

Factor	High	Low
Pressure	500 bar	100 bar
Temperature	150℃	40℃
Particle size	63-125 µm	<63 µm

In the 2^3 design, 8 combinations of factor levels were generated. Each combination was carried out in duplicate for a total number of 16 runs. Using Minitab software, randomized experimental design shown in Table 5 was generated:

Table 5: 2^3 factorial design

Run order	Temperature (℃)	Pressure (bar)	Particle Size Range (µm)
1	40	500	63-125
2	40	100	<63
3	150	500	63-125
4	150	100	<63
5	150	100	63-125
6	40	500	<63
7	40	100	63-125
8	150	500	<63
9	150	100	<63
10	40	500	<63
11	40	100	<63
12	150	500	<63
13	150	500	63-125
14	150	100	63-125
15	40	500	63-125
16	40	100	63-125

The supercritical fluid extraction was carried out according to the experimental design summarized in Table 5. The temperature and pressure were set using the controller of the supercritical fluid extraction set up as previously described. Yield was expected to increase with increasing volume of CO_2 until no more oil can be extracted. In order to examine the behavior of increasing yield with increasing CO_2 volume, weight measurements of the amount of oil collected were taken periodically. The response selected for analysis of variance was the final yield.

2.2.3.1.1 Statistical Analysis of 2^3 Design

The 2^3 factorial design was used to judge the significance of parameters and their interactions on the response. P values were used to determine the significance of factors. All factors or factor interactions with a p value < 0.05 were considered significant. Fitness and significance of the model were verified by analysis of variance (ANOVA). Minitab was used to perform the statistical analysis at 95% confidence, and generate the regression equation and all figures. In ANOVA tables the abbreviations DF, Adj SS, and Adj MS are used for degrees of freedom, adjusted sum of squares, and adjusted mean squares respectively. The model was further refined by removing any insignificant parameters and interactions.

For a 2^3 factorial design, the regression model was in the general form of: $y = \beta_{o+}\beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + \beta_{123} x_1 x_2 x_3 + \epsilon$, where x_1, x_2, x_3 refer to the factors and ϵ refers to the error (Montgomery, 2013).

2.2.3.2 RSM Design for Adsorption Experiments

One of the shortcomings of previous adsorption studies using date pits is that many of them used the one factor at a time (OFTAT) method, which fails to display interaction among factors. It fails to illustrate if the level of a certain factor, which is held constant, has an effect on the response. Displaying interactions among factors is among the advantages of Response Surface Methodology.

Response surface methodology was applied to come up with an experimental plan. Among the advantages of RSM is that it allows for the evaluation of the significance of the effect of the factors being studied on the response. It also allows for the investigation of any interactions among the factors. In addition, this method can be used to produce a statistical model that relates the response to the factors. The response optimizer tool can be used to optimize the response.

Based on the results of screening experiments, it was found that the factors pH, adsorbent dose, and time were significant parameters that affect the adsorption capacity. The results of the pH screening experiment indicated that adsorption was highest at pH 4, which was used as the optimal pH in all succeeding adsorption experiments. A Response Surface Methodology (RSM) design was prepared with Pb concentration, adsorbent dose, and time as the continuous factors; and adsorbent type as a categorical factor. Box-Behnken design was found to be most appropriate for this set up. The levels selected for lead concentration were based on a literature survey. The adsorbent dose levels were decided based on both the literature survey and the results of screening experiments. Other adsorption parameters were kept constant: pH was constant at 4, temperature at 25℃, shaking rate at 150 rpm, and particle size at <63 μm.

Among the advantages of RSM is that it allows for the evaluation of the effect of parameters on the response, as well as the interactions among parameters, which cannot be done by changing one factor at a time. In addition, RSM allows for the evaluation of parameters by testing the response at a high level, low level, and intermediate level; thus lowering the number of runs needed to evaluate a specific parameter. RSM is also useful in obtaining the set of conditions that would give the optimum response while considering all factors and interactions. Table 6 outlines the factors and levels used to generate the RSM design shown in Table 7.

Table 6: Factors and levels used in RSM design generation

Factor	Adsorbent dose (g/mL)	Pb concentration (ppm)	Time (h)	Adsorbent type
Low	0.004	10	1	R-DP
High	0.012	200	10	S-DP
				CO_2DP

Table 7: RSM design for adsorption experiments

Run Order	Dose (g/mL)	Pb concentration (ppm)	Time (h)	Adsorbent type
1	0.008	105	5.5	R-DP
2	0.004	105	10	R-DP
3	0.004	105	1	S-DP
4	0.012	10	5.5	CO_2-DP
5	0.008	200	10	S-DP
6	0.008	105	5.5	S-DP
7	0.012	200	5.5	S-DP
8	0.012	105	10	S-DP
9	0.012	105	10	CO_2-DP
10	0.012	10	5.5	S-DP
11	0.004	200	5.5	R-DP
12	0.008	105	5.5	S-DP
13	0.008	105	5.5	CO_2-DP
14	0.008	200	1	CO_2-DP
15	0.004	105	1	CO_2-DP
16	0.012	105	1	S-DP
17	0.008	10	1	CO_2-DP
18	0.008	105	5.5	R-DP
19	0.008	200	10	CO_2-DP
20	0.008	10	10	R-DP
21	0.012	105	1	CO_2-DP
22	0.004	10	5.5	R-DP
23	0.012	10	5.5	R-DP
24	0.004	105	1	R-DP
25	0.004	200	5.5	S-DP
26	0.008	10	10	S-DP
27	0.008	10	1	S-DP
28	0.008	200	1	R-DP
29	0.008	105	5.5	S-DP
30	0.008	105	5.5	R-DP
31	0.004	105	10	S-DP
32	0.008	105	5.5	CO_2-DP
33	0.012	200	5.5	R-DP
34	0.004	10	5.5	CO_2-DP
35	0.012	105	10	R-DP
36	0.008	10	1	R-DP
37	0.004	10	5.5	S-DP
38	0.008	105	5.5	CO_2-DP
39	0.004	105	10	CO_2-DP
40	0.004	200	5.5	CO_2-DP
41	0.012	200	5.5	CO_2-DP
42	0.008	200	1	S-DP
43	0.008	200	10	R-DP
44	0.012	105	1	R-DP
45	0.008	10	10	CO_2-DP

2.2.3.2.1 Statistical Analysis of RSM Box-Behnken Design

Minitab was used for statistical analysis, regression modeling, and generation of all plots. A confidence level of 95% was used. Fitness and significance of the model were verified by analysis of variance (ANOVA). Any factors or interactions with a p-value <0.05 were considered insignificant. The general regression model followed for Box-Behnken Design is the second order model shown in equation (6), where y is the response and x_1, x_2 refer to the factors and ϵ refers to the error (Montgomery, 2013).

$$y = \beta_{o+}\beta_1 x_1 + \beta_2 x_2 + \beta_{12} x_1 x_2 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \epsilon \qquad (6)$$

2.2.4 Characterization Methods

In order to better understand the nature of the adsorbents, and the details of the extraction and adsorption processes, some characterization methods were performed on the adsorbent powders: R-DP, S-DP, and CO_2-DP, as well as the oil extracted.

2.2.4.1 GC Analysis

In order to analyze the fatty acid profile of the collected date seed oil, gas chromatography was used. The oil samples from 3 different extraction processes were collected for GC analysis: Soxhlet extraction obtained by the method described in section 2.2.1.1; SC-CO_2 extraction at 500 bar, 40℃, <63 µm; and SC-CO_2 extraction at 500 bar, 150℃ , <63 µm.

In order to break the heavy fatty acids down to volatile fatty acids transesterification was performed. Firstly, 1 mL of 0.5 M methanolic KOH was added to a drop of oil sample. It was shaken well and heated in an oven at 80℃ for

10-15 minutes. Next 2 mL of 15% BF_3 in methanol was added to the mixture, which is then heated again at 80°C for 10 minutes. Then 2 mL of hexane was added to the mixture, shaken, and then allowed to settle. The top hexane layer, which contained the extracted FAME (fatty acid methyl acetate) components, was then analyzed in the GC.

For the analysis, a gas chromatograph (Shimadez, GC-2010, and Japan) equipped with a flame-ionization detector (FID) and Famewax capillary column was used. The column had a length of 30 m, film thickness 0.25 μm, and inner diameter 0.32 mm. The column oven temperature was set to 40°C then heated at a rate of 4°C/min to 240°C after a holding period of 3 minutes. Helium was used as carrier gas at a flow rate of 40 $mLmin^{-1}$ and the detector make up gas flow rate was set to be at 30 $mLmin^{-1}$. The injector temperature was set to 300°C. Total run time was 53 minutes.

2.2.4.2 TGA

TGA analysis was performed on samples of R-DP, S-DP, and CO_2-DP using TA Instruments Q500 Thermogravimetric Analyzer (TGA). The samples were heated with a fixed heating rate of 20°C/min until 800°C. About 5 mg of each sample was used for analysis.

2.2.4.3 IR Spectroscopy

FTIR spectroscopy (Shimadzu, IR-Prestige-21) was used to determine the main functional groups of R-DP, S-DP, and CO_2-DP in the range of 400-4000 cm^{-1}. About 10 mg of each sample was ground and mixed with 200 mg of KBr then pressed into pellets. The pellets were then analyzed with FTIR spectrometer.

2.2.4.4 Surface Area and Porosity Analysis

N_2 adsorption was used to calculate the BET surface area of R-DP, S-DP, and CO_2-DP and analyze their porosities. This was carried out with Micrometrics Tristar II plus surface area and porosity analyzer.

2.2.4.5 Scanning Electron Microscopy

Scanning Electron Microscopy was used to examine the surfaces of R-DP, CO_2-DP, and S-DP. A JEOL-JSM 6390A microscope, coupled with energy-dispersive X-ray (EDX) was used. Samples were sputter-coated with a thin gold layer and examined in high-vacuum mode at 15 kV and a magnification of 2000.

Chapter 3: Results and Discussion

3.1 Results of Soxhlet Extraction

The Soxhlet extraction process was carried out in duplicate with the apparatus described in section 2.2.1.1. As previously discussed, petroleum ether has been shown to be an effective solvent for extracting oil from date pits and was chosen for this study.

The average yield obtained based on two replicates was found to be 10.325 ± 0.004 %. This result agrees closely with the 10.5% reported by Hossain et al. (2014) for Khalas date pit oil. Soxhlet extraction with an appropriate solvent removes the entire lipid content of the date pits. Other yields obtained for Soxhlet extraction of date pits include 10.19% and 12.67% obtained by Besbes, Blecker, Deroanne, Drira, et al. (2004) from Deglet Nour and Allig cultivars respectively. These two cultivars were collected from Tunisia and their oil was extracted with petroleum ether as well. Ali et al. (2015) was able to obtain a yield of 8.5% from the Iraqi Zahidi cultivar with n-hexane.

3.2 Results of Supercritical Fluid Extraction

As summarized in Table 4 and Table 5 in section 2.2.3.1, a 2^3 factorial design was carried out in order to evaluate the effects of pressure, temperature, and particle size on supercritical carbon dioxide extraction of date pits. Table 8 outlines the extraction conditions and respective amount of extract and yield obtained from each. The amount extracted was recorded after passing 300 mL of supercritical CO_2. Consequently, the yield is reflective of the yield obtained after the passing of 300 mL of supercritical CO_2. The factor combinations and run order were set by the 2^3 factorial design generated in Minitab.

3.2.1 Behavior of Extraction with Increasing CO_2 Amount

In order to observe the effect of CO_2 amount on the extract yield, weight of the extract was periodically taken while increasing the amount of CO_2 passed. This was done while running the extraction conditions summarized in Table 5. The following figures display the yield verses the weight of CO_2 passed in g. Figure 3 shows the extraction results for extractions carried out at 40°C, while Figure 4 displays the results for extractions carried out at 150°C. The extract weight eventually becomes constant and does not increase with increasing CO_2. The amount of extract was found not to increase after 300 mL of CO_2 passed. Therefore, 300 mL of CO_2 was passed during the extraction runs performed as per the conditions presented in Table 5.

For the extraction run at 40°C, 500 bar, and <63 µm, stability in the yield is achieved at nearly 100 g CO_2, as shown in Figure 3. More fluctuations are observed for 40°C, 500 bar, and 63-125 µm, but still stability is eventually achieved. However at a low pressure of 100 bar, for both temperatures, the yield is nearly 0 g. The yields produced by both 40°C and 150°C at 500 bar are similar, indicating that temperature does not have a strong effect on the extraction yield.

It is clear from Figure 3 and Figure 4 that the pressure has the most significant impact on extraction yield. In fact extractions run at the low pressure of 100 bar resulted in yields of almost 0%. This is true of both temperature and particle size levels, which indicates that temperature and particle size did not have a significant effect of the yield. However, smaller particle size seems to result in smoother curves, indicating less fluctuation and better mass transfer. Furthermore, 40°C achieves slightly better yields than 150°C at lower pressure. At higher pressures a much more visible and considerable amount of extract was collected. This was an indication that pressure is the most important parameter which controls the amount of extract. This conclusion was further reinforced upon performing analysis of variance (ANOVA) on the data collected.

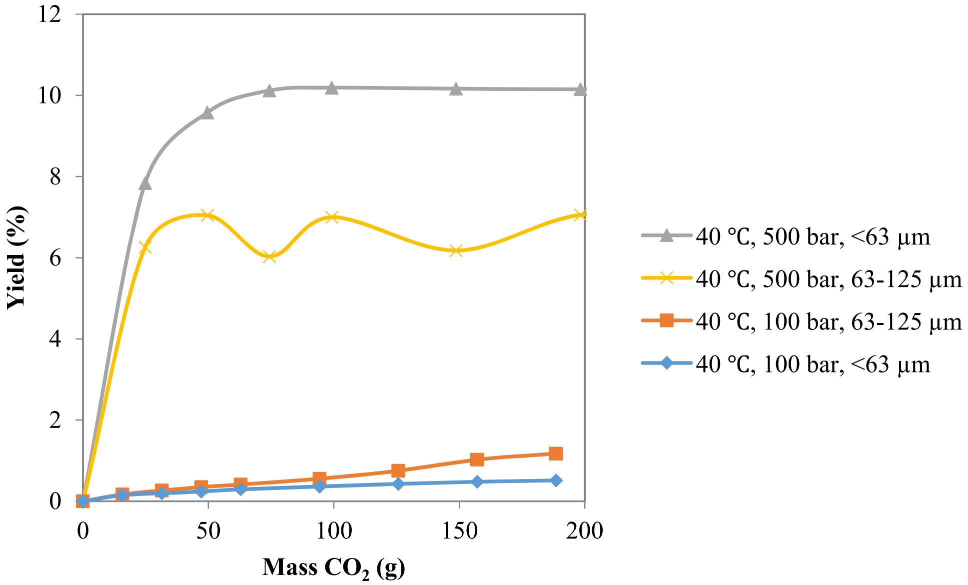

Figure 3: Yield verses weight of CO_2 passed for extractions at 40°C

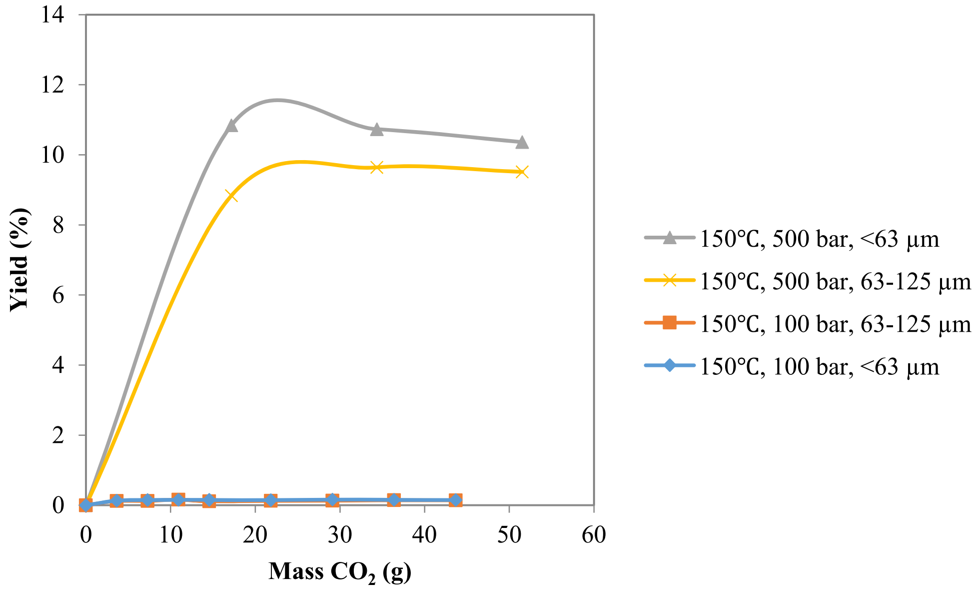

Figure 4: Yield verses weight of CO_2 passed for extractions at 150°C

3.2.2 Analysis of Variance

The percent yield at 300 mL was used as the response when performing ANOVA and was calculated using equation (1) in section 1.4.6.2.

Table 8: Results of SC-CO_2 extraction of date seed oil

Run order	Temperature (°C)	Pressure (bar)	CO_2 density (g/mL)	Particle Size (μm)	Extract weight (g)	Yield (%)
1	40	500	0.99	63-125	0.27	9.06
2	40	100	0.63	<63	0.013	0.35
3	150	500	0.69	63-125	0.28	9.34
4	150	100	0.15	<63	0.0050	0.16
5	150	100	0.15	63-125	0.0022	0.0733
6	40	500	0.99	<63	0.30	9.94
7	40	100	0.63	63-125	0.04	1.14
8	150	500	0.69	<63	0.30	10.17
9	150	100	0.15	<63	0.0040	0.14
10	40	500	0.99	<63	0.29	9.85
11	40	100	0.63	<63	0.02	0.68
12	150	500	0.69	<63	0.33	10.55
13	150	500	0.69	63-125	0.30	9.95
14	150	100	0.15	63-125	0.0066	0.21
15	40	500	0.99	63-125	0.29	9.67
16	40	100	0.63	63-125	0.04	1.21

As previously mentioned, the factorial design included 2 replicates of 8 conditions. The ANOVA method of analysis is a convenient way to evaluate the significance of parameters and quantify the impact they have on the response. In ANOVA tables the abbreviations DF, Adj SS, and Adj MS are used for degrees of freedom, adjusted sum of squares, and adjusted mean squares respectively. It is also used to build a statistical model that represents the relationship between the response and the input factors. The fit of the statistical model to the data may be examined by R^2. An R^2 value of above 80% indicates a good fit of the model to the experimental data. In addition, the response optimizer tool in Minitab is useful in determining the optimum value of parameters based on the statistical model. During this analysis any factor with a p-value less than 0.05 was considered significant. Table 9 summarizes the analysis of variance obtained from Minitab. The temperature and particle size have p-values of 0.512 and 0.557, which are higher than the significance criterion of 0.05. Therefore, temperature and particle size are insignificant factors; they do not impact the response to a significant degree. The pressure, however, is a significant factor as indicated by its p-value of 0, which indicates that pressure has a very strong effect on the yield. In fact, out of the parameters evaluated, only pressure was found to be significant.

Table 9: ANOVA summary

Analysis of Variance					
Source	DF	Adj SS	Adj MS	F-Value	P-Value
Regression	3	347.86	115.95	497.35	0
T	1	0.11	0.11	0.46	0.512
P	1	347.67	347.67	1491.23	0
Particle Size	1	0.09	0.09	0.36	0.557
Error	12	2.80	0.23		

A study conducted by H. Liu et al. (2013) investigated the effects of certain parameters on the yield of extract from date pits. The parameters studied included pressure (bar), temperature, extraction time, and number of extraction times in an orthogonal array design. They used crushed date pits in the particle size range 53-425 µm. In addition, the authors used ethanol as a cosolvent with the supercritical CO_2. These parameters and conditions differed slightly from those used in this study. Also no cosolvent was used with the supercritical CO_2 in this study.

The ANOVA result of the study by H. Liu et al. (2013) which evaluated pressure, temperature, extraction time, and number of extraction times showed that the only significant parameter was number of extraction. Pressure, temperature, and extraction time were found to be insignificant.

It is clear that the findings of this study differ from the findings of H. Liu et al. (2013), as pressure was found to be the most significant factor in this study. Pressure, is an important parameter as it allows for more carbon dioxide per area and better diffusion. In addition, the density of SC-CO_2 increases with increasing pressure. As the density of SC-CO_2 increases, its power as a solvent increases. H. Liu et al. (2013) explained that date seeds were so hard that pressure may not exert a significant effect on the extract. The results found by H. Liu et al. (2013) differ with other reports. Gelmez, Kıncal, and Yener (2009) and J. Liu et al. (2011) reported that pressure was the most significant factor on amount of extract collected by supercritical fluid extraction of roasted wheat germ and corn silk respectively. Results of this study are in agreement with their findings, showing that pressure is the most important factor.

In addition to determining the significant factors, ANOVA can also be used to derive a statistical model. Table 10 displays the coefficients of every factor as calculated by Minitab, the regression equations, the R^2 value for the model. The R^2 value, 99%, indicates that the statistical model is a good fit to the experimental data analyzed. The regression equation is a statistical model that represents the relationship between % yield and the temperature and pressure for each particle size range. The effect of particle size at the two ranges investigated was found to be insignificant. The two levels chosen for particle size are probably too close together to allow a significant effect of particle size to be seen. This is in an effort to work with the smallest possible particle sizes in order to allow for best extraction, and in the next stage, best adsorption. Both extraction and adsorption are enhanced at smaller particle sizes. Since particle size is a categorical factor, Minitab produces a statistical model that relates % yield to temperature and pressure for each particle size range separately, as displayed in Table 10. The models presented for both ranges are very similar, which further confirms the conclusion that particle size is an insignificant parameter.

Table 10: Regression equation obtained for yield in terms of extraction parameters

Regression Equation	
Particle Size **63-125 µm**	yield = -1.77 - 0.0015 T + 0.023 P
<63 µm	yield = -1.62 - 0.0015 T + 0.023 P
R-sq	99.20%

In addition to the R^2 value, the statistical model can further be assessed by analyzing the residual plots shown in Figure 5. The normal probability plot shows that the assumption of linearity is valid. The residual verses fit plot indicates constant variance, and the random nature of the residual verses observation order indicates independence. Therefore, this is a dependable model and it fits well to the general linear model. This statistical model provides a relationship between the expected % yield given the temperature, pressure, and particle size range.

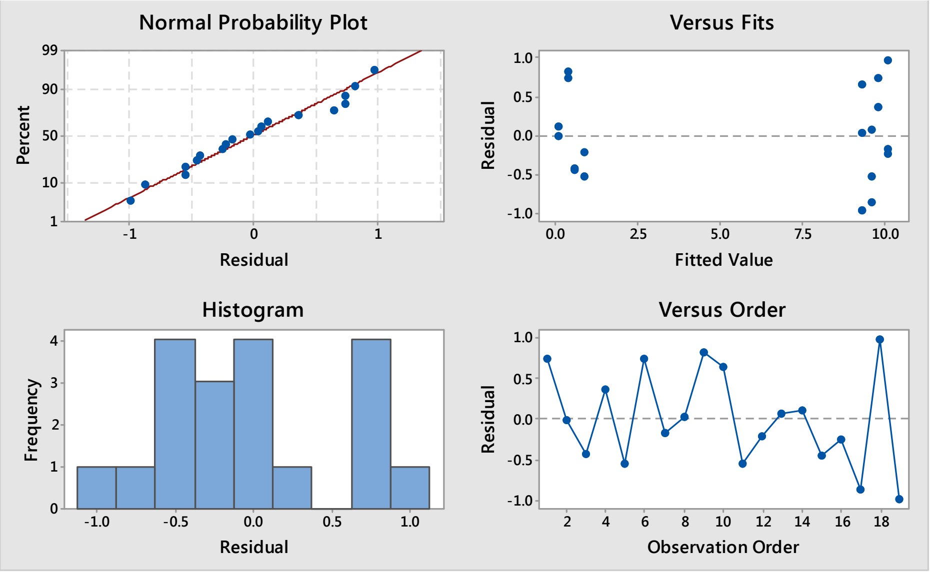

Figure 5: Residual plots

3.2.3 Experimental Testing of the Model

In order to test the model presented in Table 10, three sets of conditions were selected and tested. Extractions were carried out at 60°C, 400 bar, 63-125 µm; 80°C, 200 bar, 63-125 µm; and 70°C, 400 bar, <63 µm. The experimental results obtained from these test points were then compared to the values predicted by the statistical model.

The yield (%) of the test points chosen closely resemble the values predicted by the statistical model presented. The % difference between the predicted and experimental values is calculated as shown in equation (7). The average % difference was found to be 13.138%, which indicates that the model can be relied on to make predictions. It can be used for predicting the yield (%) given the temperature, pressure, and particle size for this particular set up.

$$\% \, difference = \frac{|predicted - experimental|}{\frac{predicted + experimental}{2}} \quad (7)$$

The variations between predicted and experimental values might be due to the fact that consistent performance of the ISCO SFX Extractor is difficult to achieve, due to the blockage in the pipes. It is possible that oil is deposited in the exit pipes while being carried out by CO_2, despite cleaning with hexane between runs. In addition it is difficult to get a consistent performance from the ISCO SFX Extractor as the exit flow rate tends to decrease with time and must be manually adjusted in order to stay at the set point. Since the flow rate needs to be manually controlled, it is therefore subject to ups and downs. The flow rate has a tendency to increase very fast when opening the exit valve and slowing down too low too soon after adjusting the flow rate to the desired level. These inconsistent highs and lows can lead to inconstant weight readings. When the flow rate is high more oil tends to be released and more frozen CO_2 is collected on the collection vial. Since each run is subject to these highs and lows in an inconsistent way, replicates may not be exactly the same. Also, when the entire volume of CO_2 in the syringe pipe has been consumed, the extraction stops in order for the pump to refill. It could happen at any point in the extraction process, and not always at the same point in every run. The fluctuations in the flow may affect the extraction results.

3.2.4 Effect of Pressure

Figure 6 illustrates the pressure effect on the extraction yield. It is apparent that the pressure has quite a strong effect on the extraction yield. As previously discussed, increasing the pressure increases the density of SC-CO_2, which increases its power as a solvent. As confirmed by ANOVA, having a higher pressure will result in a significantly higher yield. This was found to be true at both temperature and particle size levels. As shown in Figure 3 (section 3.2.1), for a temperature of 40°C and particle size <63 μm, the yield was only 0.51% at 200 g CO_2; however it is nearly 10 times that amount (10.15%) at 500 bar for the same temperature, particle size, and mass of CO_2. That same pressure effect is also observed for extraction conditions at 150°C and 63-125 μm. As shown in Figure 4 (section 3.2.1), the yield at 100 bar, 150°C, 63-125 μm at 40 g CO_2 was only 0.14%, whereas it was 9.5% at 500 bar for the same temperature and particle size. Figure 6 further illustrates the effect of pressure of extraction yield.

As previously mentioned, temperature has competing effect on the yield. On the one hand, increasing temperature decreases the density which reduces the solvent power of CO_2. However, increasing temperature also increases the volatility of the solutes. At a certain pressure, known as the crossover pressure, the temperature effect on density becomes less dominant, and its effect on volatility becomes more dominant. As shown in Figure 3 and Figure 4, at low pressure lower temperature achieves a slightly better yield than high temperature. This is to be expected, since at pressures below the crossover pressure having low temperature is favorable because low temperature increases the density, which increases the solvent power, thus achieving a higher yield. Solubility studies are needed to confirm the value of the crossover pressure.

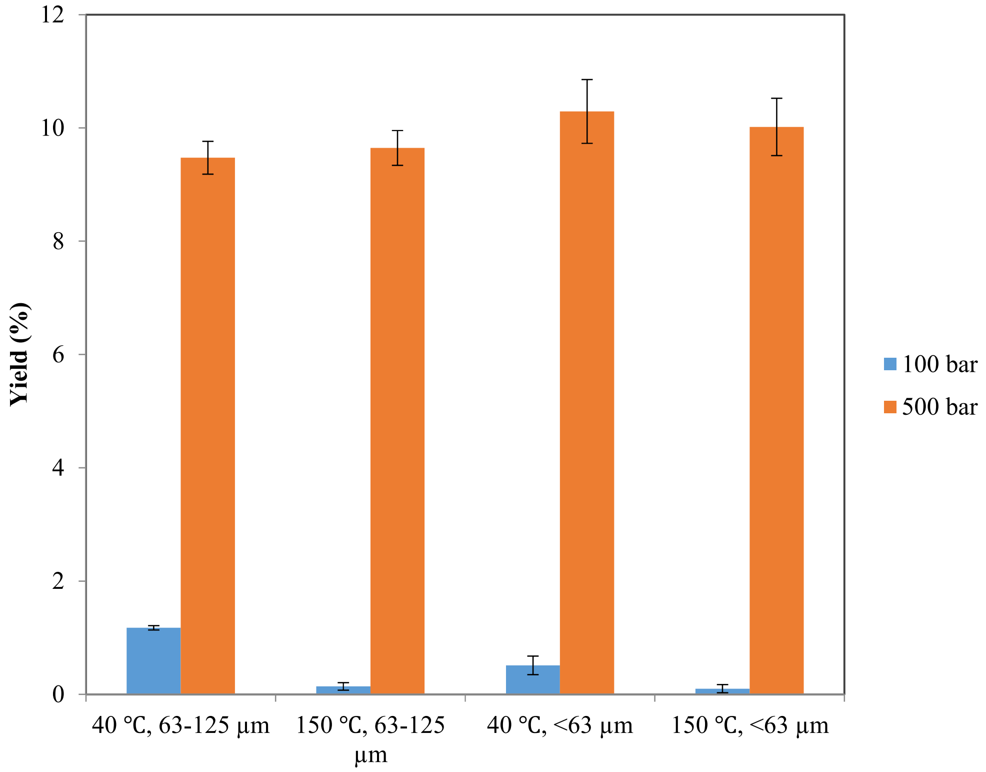

Figure 6: Effect of pressure on extraction yield

3.2.5 Effect of Temperature

As previously concluded from ANOVA, temperature was not found to have a significant effect on % yield. This conclusion is further reinforced graphically in Figure 7. The % yield does not change to a significant degree with changing temperature. The effect of temperature at pressures below the crossover pressure is that lower temperature leads to higher density and higher yield. In other words, at pressures below the crossover pressure, lower temperatures result in higher yields due to the dominating density effect. This can be seen in Figure 4 where at 150℃, 100 bar, 63-125 µm, and about 40 g CO_2 the yield was 0.14%. However at the lower temperature of 40°C and the same pressure, particle size, and CO_2 weight, more than double the yield was achieved (0.35%).

At higher temperatures, the solute is more volatile, which leads to higher diffusion into the solvent. As shown in Figure 3 and Figure 4, at high pressure, higher temperature achieves a slightly higher yield; this is due to the dominating volatility effect. In Figure 3 at 40°C, 500 bar, 63-125 µm, and about 20 g CO_2 the yield was 6.25%. However the yield was slightly higher (8.83%) at the higher temperature of 150°C and the same pressure, particle size, and CO_2 weight. Figure 7 illustrates the effect of temperature as a bar chart.

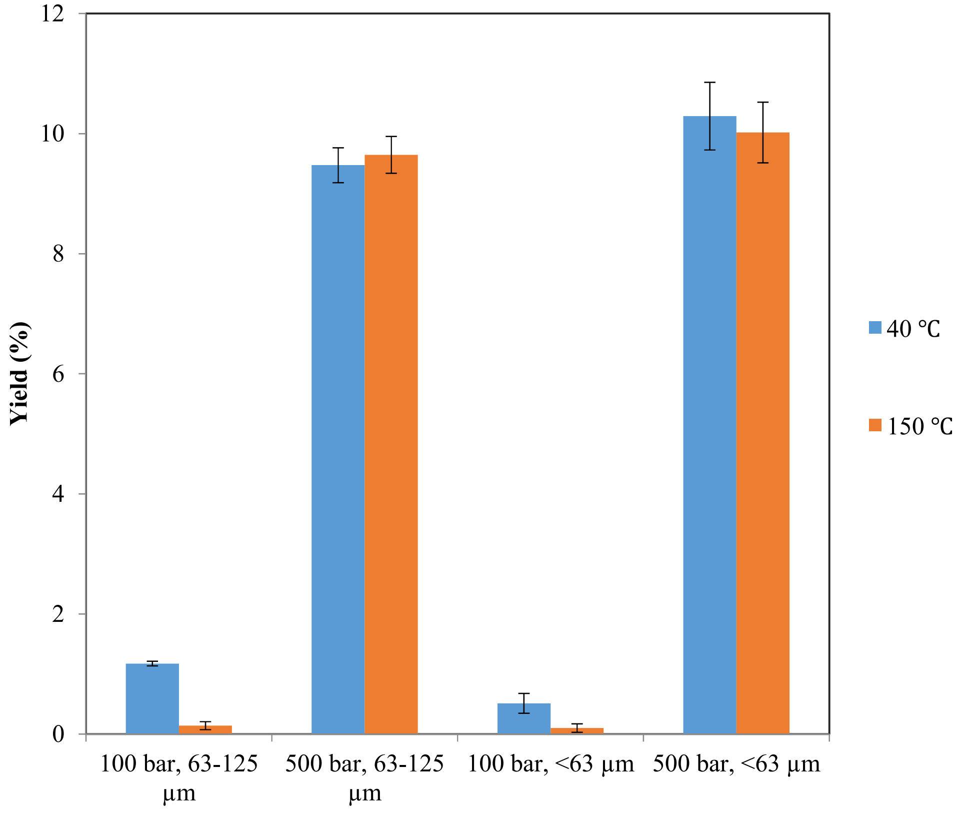

Figure 7: Effect of temperature on extraction yield

3.2.6 Effect of Particle Size

Smaller particle sizes result in larger surface areas. Therefore, it was expected that the smaller particle size would result in higher yield, since it allows for a larger mass transfer area of the solute into the SC-CO_2. However ANOVA confirmed that for the two ranges studied (63-125 µm and <63 µm) particle size was not found to have a significant effect. This can also be seen in Figure 3 and Figure 4, where a smaller particle size gives only a slightly higher yield. For example, at about 35 g CO_2 the yield at 500 bar, 150°C, <63 µ was 10.73%, only slightly higher than the 9.64% obtained for the same pressure, temperature, and CO_2 weight and particle size 63-125 µm. Figure 8 further illustrates the effect of particle size. The smaller of the two ranges, <63 µm, was selected for the batch adsorption experiments to follow, since smaller particle size results in increased surface area and more active pores for adsorption sites (Al-Ghouti et al., 2010).

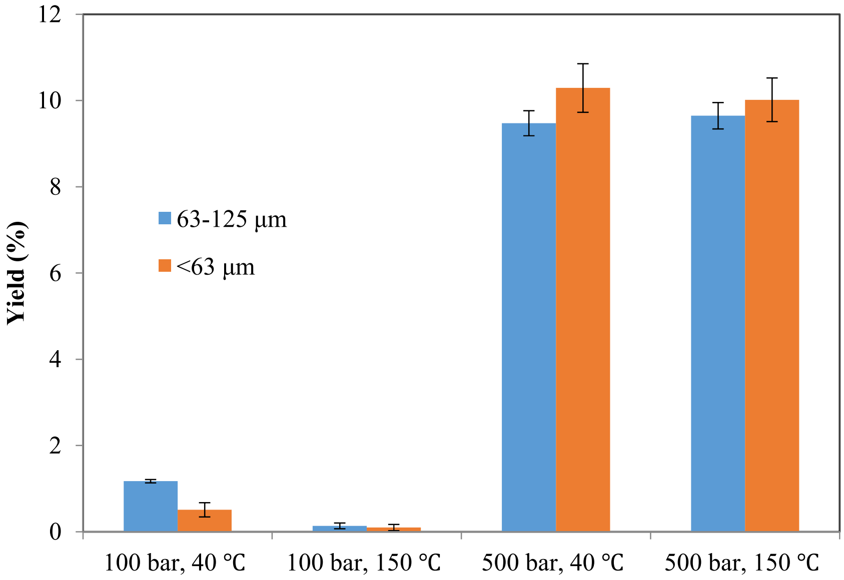

Figure 8: Effect of particle size on extraction yield

3.2.7 Optimal SC-CO_2 Extraction Conditions

After confirming the adequacy of the model experimentally, the response optimizer tool in Minitab was used to statistically determine the optimum conditions. The yield was maximized and the optimum conditions were found to be: temperature 150°C, pressure 500 bar, and particle size <63 µm. However, since temperature was found to be an insignificant parameter, it was decided that the extra energy needed for 150°C was not worth the very minimal increase in the yield that may come with increased temperature. Hence, it was decided to consider the conditions temperature 40°C, pressure 500 bar, and particle size <63 µm as the optimum conditions. The powder residue from this extraction condition was used to perform adsorption experiments, in addition to the solid residue from Soxhlet extraction and raw date pit powder. The adsorption capacity for each adsorbent was then compared.

3.2.8 Summary of Soxhlet and SCF Extraction

Table 11 summarizes the average yields obtained by both Soxhlet and SCF extraction methods. Both methods give the same yield. In addition, the extraction yields obtained by both Soxhlet (10.3%) and SCF extraction (10.29%) are very similar to the literature value of 10.5% (Hossain et al., 2014) for Khalas date pits. This indicates that supercritical carbon dioxide extraction is just as effective as the traditionally used Soxhlet extraction for extraction of lipids from date pit powder. Hence supercritical carbon dioxide extraction can be used to extract date pit oil without compromising the yield. It is preferable to use supercritical carbon dioxide extraction since it allows higher selectivity, and is more environmentally friendly compared to organic solvents. In addition, supercritical carbon dioxide extraction does not require an additional separation process to separate the solvent from the extract, as the CO_2 is immediately separated from the extract upon the release of pressure.

Table 11: Summary of extraction yields

	Soxhlet	Optimal SC-CO_2 extraction conditions	Literature value of Khalas date pit oil (Hossain et al., 2014)
Average yield (%)	10.3 ± 0.035	10.29 ± 0.56	10.5

3.2.9 GC Analysis of Oil Samples

Three samples of oil extracted from date pits were analyzed using gas chromatography. One oil sample was obtained from Soxhlet extraction with petroleum ether, as detailed in section 2.2.1.1. The second sample was obtained from SC-CO_2 extraction at temperature 40℃, pressure 500 bar, particle size <63 µm. The third sample was obtained from SC-CO_2 extraction at temperature 15 ℃, pressure 500 bar, particle size <63 µm. The main fatty acid components of these samples are summarized in Table 12.

As shown in Table 12, the main difference between the extraction methods is that the oil sample from Soxhlet extraction contained C14:0 whereas the oil samples from SC-CO_2 extraction did not. In addition, the oil samples obtained from SC-CO_2 extraction contained C13:0 and C18:0, while the oil from Soxhlet extraction did not. However the extraction temperature of SC-CO_2 did not have an effect on the composition of the oil samples, as the fatty acid profiles of both oils extracted by SC-CO_2 are nearly identical.

These results show that SC-CO_2 has different selectivity than traditional organic solvents. The fatty acid profile obtained for the oil sample from Soxhlet extraction is similar to the fatty acid profiles obtained by other researchers who extracted date pit oil with traditional solvents, as shown in Table 12. Amani, Davoudi, Tahvildari, Nabavi, and Davoudi (2013) reported the fatty acid profile for date pit oil of unknown cultivar. Ali et al. (2015) reported the fatty acid profile obtained from the Soxhlet extraction of Iraqi Zahidi date pits. Al-Hooti, Sidhu, and Gabazard (1998) reported the fatty acid profile of date pit oil from local UAE cultivars, while Al-Shahib and Marshall (2003) have reported the fatty acid profile of many cultivars, that of Safawy date pit oil is presented in Table 12.

In this study, Oleic Acid, C18:1, was found to be most abundant component. It was found to be 49.92% for the sample obtained by SC-CO_2 extraction at 40℃, 500 bar, <63 µm; 49.67% for the sample obtained by SC-CO_2 extraction at 150℃, 500 bar, <63 µm; and 53.64% for the sample obtained from Soxhlet extraction. This result is in agreement with Al-Shahib and Marshall (2003) who reported 49.9% C18:1 for date pit oil of Safawy dates and Ali et al. (2015) who reported 51.46 % C18:1.

Table 12: Fatty acid profiles of oils obtained from different extraction methods

Fatty Acid (%)	Lauric (C12:0)	Tridecanoic (C13:0)	Myristic (C14:0)	Palmitic (C16:0)	Stearic (C18:0)	Oleic (C18:1 (Cis))	Linoleic (C18:2 (Cis))
SC-CO_2 extraction at 40℃, 500 bar, <63 μm	15.94	11.07		11.31	2.76	49.92	6.62
SC-CO_2 extraction at 150℃, 500 bar, <63 μm	15.87	11.11		11.60	2.61	49.67	6.62
Soxhlet extraction	15.32		10.76	11.21		53.64	6.53
Ali et al. (2015)	11.36		11.45	13.85	6.56	51.46	
Amani et al. (2013)	24		13	17.44		36.8	7
Al-Hooti et al. (1998)	8.3		6	11.9	2.6	56.1	11.6
Al-Shahib and Marshall (2003)	11.2		10.5	12.2	4.1	49.9	9.1

3.3 Adsorption Experiments

The powder residues from the Soxhlet extraction (S-DP), SC-CO_2 extraction at 40℃, 500 bar, <63 μm (CO_2-DP), and raw date pits (R-DP) were used as adsorbents to remove lead from aqueous solution. All powder residues used were selected from the particle size range <63 μm in order to allow for the most surface area.

One objective of this research was to see if the extraction of lipids from date pit powder has any effect on its adsorption ability. Therefore, the adsorption capacity of three different adsorbents derived from date pits (R-DP, S-DP, and CO_2-DP) was compared. Lead was chosen as the solute for the purpose of this study, since lead is one of the most widespread and toxic pollutants, and the literature showed that date pit adsorbents have an affinity to lead.

In order to achieve the aforementioned objective, batch adsorption experiments were carried out. The adsorption process is sensitive to factors including contact time, pH, adsorbent dose, particle size, temperature, and shaking rate.

Based on literature, temperature and shaking rate were found to be less significant parameters. The only importance of shaking is to provide agitation. The particle size was kept constant at the smallest possible particle size, <63 μm. The temperature was also kept constant at 25℃ throughout and the shaking rate was constant at 150 rpm.

The parameters pH and adsorbent dose were evaluated in screening experiments. During these screening experiments, only the factor being studied was changed while all other factors were kept constant. The purpose of screening experiments was to find out which factors had a significant effect on the adsorption, and to determine the levels needed to create the RSM design. Since only one factor at a time is changed, these screening experiments do not give any information about any interactions that may occur among factors, which is why RSM is needed. RSM gives a full analysis of the interaction among factors. The results of the screening experiments were used to determine the factors and factor levels of the RSM. The response of the adsorption experiments is q (mg of lead adsorbed per g of adsorbent), calculated using equation (5) in section 2.2.2.

The following sections describe the screening experiments, which were carried out in order to determine the important factors and their appropriate levels to be used in the RSM design.

3.3.1 Effect of pH

As shown in the literature review, adsorption is highly sensitive to the pH of the solution. In order to determine the optimum pH range, R-DP was used as an adsorbent for lead solutions of 10 ppm with pH ranging from 0-6, as lead precipitates at a pH of above 6. As shown in Figure 9, q was measured at each pH level.

The pH plays a very important role in the adsorption of lead onto R-DP. According to Figure 9, the pH range in which the R-DP adsorbs the most lead occurs from 3-5, with the optimum occurring at pH 4. For lead solutions with a pH of less than 3, a very negligible amount of lead was adsorbed. At around pH 3 there is a large increase in amount of lead adsorbed; about 7 times as much lead was adsorbed at pH 3 when compared to pH 2. It is believed that in solutions with low pH, which contain higher hydrogen concentration, there is competition for adsorption sites among the hydrogen and lead ions. However, as the pH increases and the hydrogen concentration decreases, there is less competition for adsorption sites by the hydrogen ions, so the adsorption sites become more accessible for the lead ions (Al-Muhtaseb et al., 2008). In addition, at low pH (below 4) it is believed that most of the carboxylic groups are protonated, therefore preventing the positively charged cations from binding to the adsorbent surface. However at higher pH, deprotonation of the carboxylic groups occurs; thus, allowing a higher negative charge density on the adsorbent, resulting in more binding of the positively charged lead ions. After the optimum pH, the adsorption capacity begins to decrease, as seen in Figure 9. This is probably due to an increase in hydroxyl ions (OH-) that may form complexes with lead ions in solution (Anantha & Kota, 2016).

Figure 9 indicates that the expected optimum adsorption occurs at pH 4. Therefore, the pH level was kept at 4 in all consequent experiments. This result is in agreement with previous studies that have used natural materials for adsorption of lead. Abu Al-Rub, El-Naas, Ashour, and Al-Marzouqi (2006) tested lead adsorption on Chlorella vulgaris, a type of algae. An optimum pH of 5 was used, which allows for lead removal without any concern of lead precipitation. This value also lies within the optimum pH range found in this study. In a study conducted by Anantha and Kota (2016) lead ions were adsorbed from solution by use of a polymer composed of waste poultry feathers and chitosan. In a one factor at a time set up, the solution pH was changed from 2 to 9 and the maximum adsorption was found at pH 4.

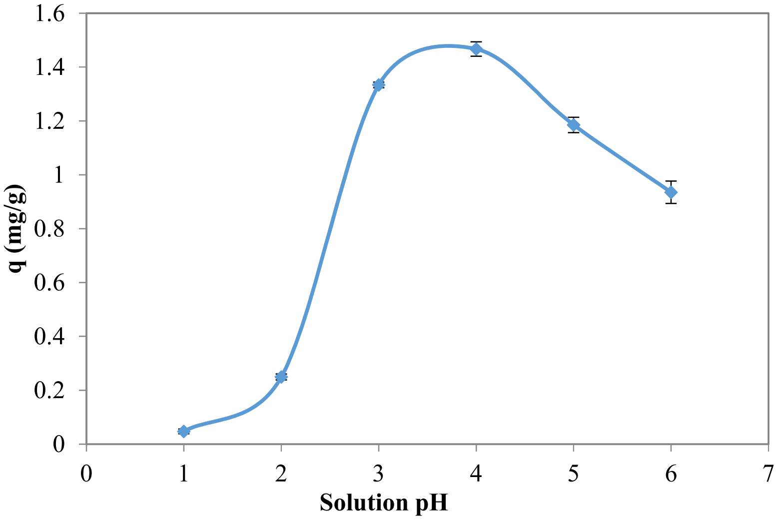

Figure 9: Adsorption capacity verses solution pH at lead concentration 10 ppm, adsorbent dose 0.008 g/mL

3.3.2 Effect of Adsorbent Dose

In addition to performing a screening experiment to determine the pH levels necessary for the RSM design, a screening experiment was also carried out to determine the appropriate levels of adsorption dose needed in the RSM design. A mass of R-DP ranging from 0.002–0.04 g/mL was investigated. The results are shown in Figure 10, where the adsorption capacity, calculated by equation (5) and the % removal is calculated by equation (8).

Figure 10 shows the behavior of both the adsorption capacity (blue line) and the % lead removal (orange line) with changing adsorbent dose. The adsorption capacity approaches infinity as the adsorbent mass gets smaller, and that is due to the mass being in the denominator of (5). Therefore, % removal was used to help determine the appropriate dose. The optimum dose was found to be 0. 008 g/mL. The lower level dose used in the RSM design was therefore 0.004 g/mL and the higher level dose was 0.012 g/mL, with the expected optimum, 0.008 g/mL, being in the middle of that range.

$$\%\ \mathrm{removal} = \frac{(c_0 - c_f)}{c_0} * 100\% \tag{8}$$

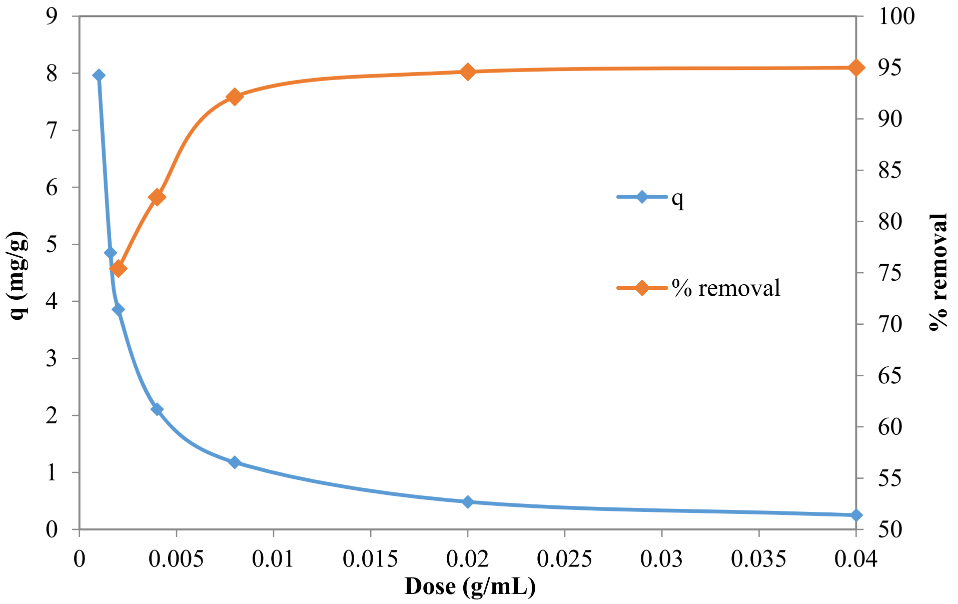

Figure 10: Adsorption capacity and % removal verses adsorbent dose for R-DP, lead concentration 10 ppm, pH 4

3.3.3 Response Surface Methodology Adsorption Experiments

3.3.3.1 (RSM) Design for Adsorption Experiments

Many adsorption studies (Al-Ghouti et al., 2010) changed one factor at a time (OFTAT). The drawback of this method is that it does not allow for the examination of second and third order factor interactions. The analysis of variance (ANOVA) carried out in this study indicates that second order interactions, including dose*dose, Pb concentration *Pb concentration , time*time, dose*Pb concentration , dose*time, Pb concentration *time are in fact significant interactions. The effect of these two way interactions can not be reflected in the data when applying one factor at a time method.

Based on the screening experiments outlined in 3.3.1 and 3.3.2 an RSM design was generated based on Box Behnken design. The continuous factors included lead concentration, adsorbent dose, and time. Adsorbent type was treated as a categorical factor. The factors and levels are summarized in Table 13.

Table 13: Factors and levels input into RSM design of adsorption experiments

Factor	Adsorbent dose (g/mL)	Pb concentration (ppm)	Time (h)	Adsorbent type
High	0.012	200	10	R-DP
Low	0.004	10	1	S-DP
				CO_2-DP

The Box Behnken design described in Table 7 (section 2.2.3.2) was carried out. The maximum time used was 10 hours. The uptake q (mg/g), which is the response of interest in this set-up, is displayed in Table 14. After carrying out the experiment, analysis of variance (ANOVA) was performed using Minitab in order to determine the statistical significance of factors, quantify their effect on the response, and identify any possible 2-way interactions. Since RSM allows for the illustration and quantification of the 2-way interactions among the factors, it has an advantage over the one factor at a time method. Furthermore, ANOVA is a tool which will help determine not only the statistical significance of adsorbent dose, lead concentration, and time; but it will also help in answering the main research question: does the extraction of lipids from date pit powder have any effect on the adsorption capacity of the powdered date pits?

Table 14: Box Behnken results

Run	Dose (g/mL)	Pb concentration (ppm)	Time (h)	Adsorbent type	q (mg/g)
1	0.008	105	5.5	R-DP	9.88
2	0.004	105	10	R-DP	11.67
3	0.004	105	1	S-DP	8.45
4	0.012	10	5.5	CO_2-DP	0.91
5	0.008	200	10	S-DP	12.86
6	0.008	105	5.5	S-DP	11.10
7	0.012	200	5.5	S-DP	12.97
8	0.012	105	10	S-DP	6.82
9	0.012	105	10	CO_2-DP	7.20
10	0.012	10	5.5	S-DP	0.91
11	0.004	200	5.5	R-DP	6.99
12	0.008	105	5.5	S-DP	11.01
13	0.008	105	5.5	CO_2-DP	11.07
14	0.008	200	1	CO_2-DP	11.41
15	0.004	105	1	CO_2-DP	9.30
16	0.012	105	1	S-DP	7.36
17	0.008	10	1	CO_2-DP	1.21
18	0.008	105	5.5	R-DP	9.40
19	0.008	200	10	CO_2-DP	13.76
20	0.008	10	10	R-DP	1.20
21	0.012	105	1	CO_2-DP	3.74
22	0.004	10	5.5	R-DP	2.03
23	0.012	10	5.5	R-DP	0.85
24	0.004	105	1	R-DP	4.81
25	0.004	200	5.5	S-DP	11.44
26	0.008	10	10	S-DP	1.26
27	0.008	10	1	S-DP	0.96
28	0.008	200	1	R-DP	8.23
29	0.008	105	5.5	S-DP	10.33
30	0.008	105	5.5	R-DP	10.25
31	0.004	105	10	S-DP	13.21
32	0.008	105	5.5	CO_2-DP	10.83
33	0.012	200	5.5	R-DP	11.94
34	0.004	10	5.5	CO_2DP	2.47
35	0.012	105	10	R-DP	7.55
36	0.008	10	1	R-DP	0.97
37	0.004	10	5.5	S-DP	2.47
38	0.008	105	5.5	CO_2-DP	11.04
39	0.004	105	10	CO_2-DP	13.38
40	0.004	200	5.5	CO_2-DP	10.99
41	0.012	200	5.5	CO_2-DP	13.80
42	0.008	200	1	S-DP	10.11
43	0.008	200	10	R-DP	13.53
44	0.012	105	1	R-DP	6.40
45	0.008	10	10	CO_2-DP	1.25

3.3.3.2 Analysis of Variance (ANOVA) for RSM of Adsorption Experiments

Minitab software was used to analyze the experimental data to generate a statistical model relating the response (uptake, *q* (mg/g)) to the experimental factors; adsorbent dose, lead concentration, and time for each adsorbent type. In addition, ANOVA allows for the examination of the main factor effects and any two way interactions that may occur among the factors. In other words, this type of analysis shows if one factor affects the response by changing another factor. It also determines which main factors and 2-way interactions are statistically significant.

P-values are used to determine which factors and interactions are statistically significant. Any p-value which is less than 0.05 indicates the significance of the factor or interaction. The ANOVA table is presented in Table 15, which displays the p-values for the main factors and the two way interactions. The main factors dose, lead concentration, and time were all found to be significant, while the adsorbent type was found to be insignificant. This conclusion is central to answering the research question. This result indicates that the extraction of oil from date pit powder has no significant effect on its adsorption capacity. In addition, the two way interactions dose*dose, Pb concentration *Pb concentration, time*time, dose*Pb concentration , dose*time, Pb concentration *time were also found to be significant, indicating that there are interactions among factors. The factor coefficients are presented in Table 16.

Table 15: ANOVA table, RSM adsorption design

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	17	845.12	49.71	27.58	0
Linear	5	678.23	135.65	75.25	0
dose	1	11.72	11.72	6.5	0.017
Pb concentration	1	615.57	615.57	341.48	0
time	1	39.34	39.34	21.82	0
Adsorbent type	2	11.61	5.81	3.22	0.056
Square	3	115.59	38.53	21.37	0
dose*dose	1	12.64	12.64	7.01	0.013
Pb concentration* Pb concentration	1	99.43	99.43	55.15	0
time*time	1	14.73	14.73	8.17	0.008
2-Way Interaction	9	51.30	5.70	3.16	0.01
dose*ppm Pb	1	15.39	15.39	8.53	0.007
dose*time	1	11.29	11.29	6.26	0.019
dose*Adsorbent type	2	9.30	4.65	2.58	0.094
Pb concentration *time	1	8.06	8.06	4.47	0.044
Pb concentration *Adsorbent type	2	4.80	2.40	1.33	0.281
time*Adsorbent type	2	2.48	1.24	0.69	0.512
Error	27	48.67	1.80		
Lack-of-Fit	21	47.92	2.28	18.24	0.001
Pure Error	6	0.75	0.13		
Total	44	893.79			

Table 16: Coded coefficients of all factors and interactions

Term	Effect	Coef	SE Coef	T-Value	P-Value	VIF
Constant		10.55	0.45	23.56	0	
dose	-1.40	-0.70	0.27	-2.55	0.017	1
Pb concentration	10.13	5.06	0.27	18.48	0	1
time	2.56	1.28	0.27	4.67	0	1
Adsorbent type						
S-DP	0.64	0.32	0.28	1.14	0.27	1.33
CO_2-DP	0.79	0.40	0.28	1.40	0.17	1.33
dose*dose	-2.14	-1.07	0.40	-2.65	0.013	1.01
Pb concentration *Pb concentration	-5.99	-3.00	0.40	-7.43	0	1.01
time*time	-2.31	-1.15	0.40	-2.86	0.008	1.01
dose*Pb concentration	2.27	1.13	0.39	2.92	0.007	1
dose*time	-1.94	-0.97	0.39	-2.5	0.019	1
dose*Adsorbent type						
S-DP	-0.48	-0.24	0.39	-0.62	0.54	1.33
CO_2-DP	-1.23	-0.61	0.39	-1.58	0.13	1.33
Pb concentration *time	1.64	0.82	0.39	2.11	0.04	1
Pb concentration *Adsorbent type						
S-DP	0.32	0.16	0.39	0.41	0.69	1.33
CO_2-DP	0.90	0.45	0.39	1.16	0.26	1.33
time*Adsorbent type						
S-DP	-0.74	-0.37	0.39	-0.96	0.35	1.33
CO_2-DP	-0.08	-0.04	0.39	-0.1	0.92	1.33

Minitab was also used to generate a statistical model relating the adsorption uptake, q, of each adsorbent to the significant factors and factor interactions, The models are presented in Table 17. The R^2 value of the model, 94%, indicates a good fit.

Table 17: Statistical adsorption models

Type of adsorbent	Statistical Model		
	R^2	R^2 (adj)	R^2 (pred)
	94.55%	91.13%	81.42%
S-DP	q = -2.55 + 32.7 dose + 0.090 Pb concentration + 1.06 time - 106.8 dose*dose - 0.00033 Pb concentration *Pb concentration - 0.057 time*time + 0.12 dose*Pb concentration - 2.155 dose*time + 0.001917 Pb concentration *time		
CO_2-DP	q = -2.46 + 29.0 dose + 0.093 Pb concentration + 1.13 time - 106.8 dose*dose - 0.00033 Pb concentration *Pb concentration - 0.057 time*time + 0.12 dose*Pb concentration - 2.1 dose*time + 0.0020 Pb concentration *time		
R-DP	q = -5.89 + 43.6 dose + 0.082 Pb concentration + 1.23 time - 106.8 dose*dose - 0.00033 Pb concentration *Pb concentration - 0.057 time*time + 0.12 dose*Pb concentration - 2.15 dose*time + 0.0020 Pb concentration *time		

The following figures represent main effects plots generated with Minitab. These plots are used to interpret how factor levels affect the response, by plotting the average response at each level of the factor, while keeping the other factors constant.

Figure 11 illustrates the effect of adsorbent dose on the adsorption uptake, q. The uptake increases slightly as the dose is increased from 0.004 to about 0.007 g/mL. After about 0.0075 g/mL the uptake decreases. This may be due to reduced mixing as a result of increased concentration of adsorbent in the solution, decreased availability of solute, electrostatic interactions, and interference between binding sites. As a result, many binding sites are left unsaturated and the uptake decreases (Abu Al-Rub et al., 2006; El-Naas et al., 2010; Fourest & Roux, 1992; Meikle, Gadd, & Reed, 1990).

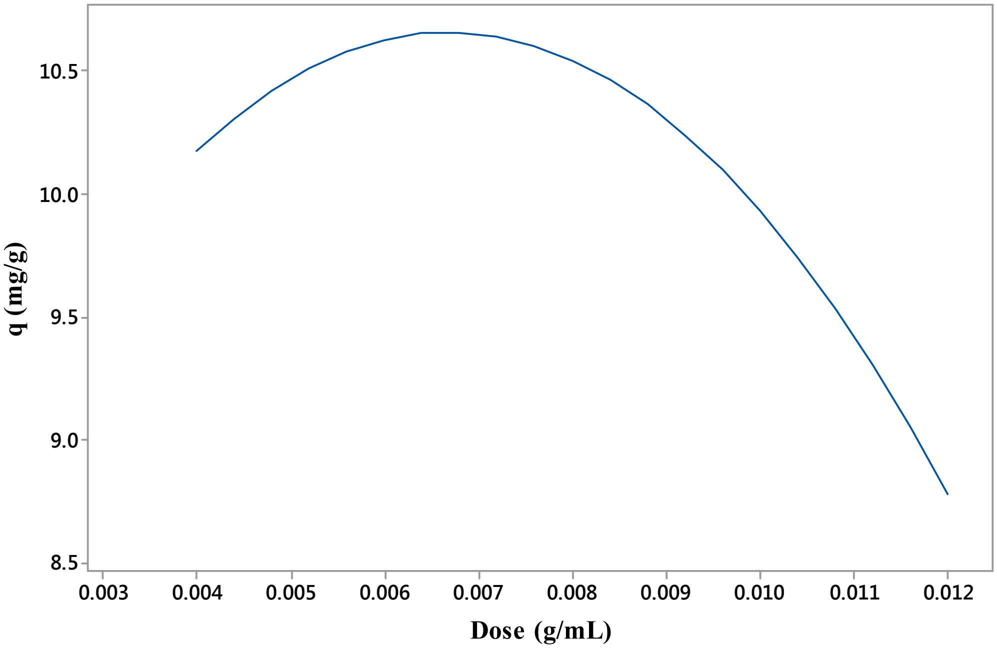

Figure 11: Effect of adsorbent dose on uptake at lead concentration 105 ppm and time 5.5 hours for CO_2-DP

Figure 12 displays the effect that lead concentration had on adsorption uptake. The uptake increases as lead concentration increases, eventually reaching a plateau. This is to be expected since, starting with a higher concentration allows more lead to be adsorbed. This result is in agreement with Samra et al. (2014), who found that increasing initial lead concentration resulted in higher uptake by the adsorbent raw date pits. This is due to higher lead concentration per unit weight of adsorbent.

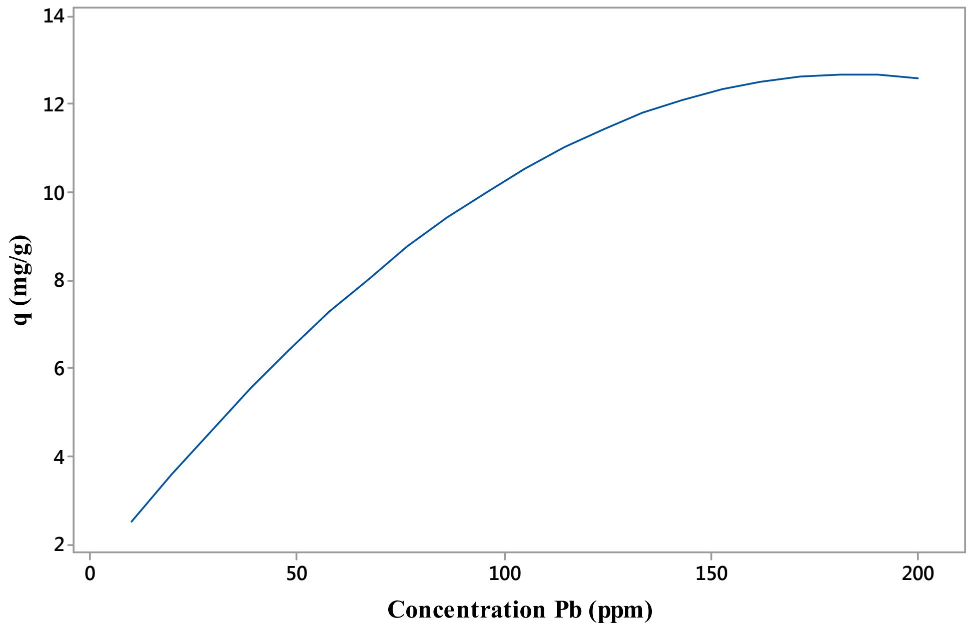

Figure 12: Effect of lead concentration on uptake for dose 0.008 g/mL, time 5.5 hours, for CO_2-DP

Figure 13 represents the effect of time on adsorption. The uptake increases with time, eventually reaching a maximum, after which no more adsorption occurs, as the surface would be completely saturated with lead ions. Adsorption progresses with time. In the initial stages of the adsorption process, adsorption happens on the surface. Then intraparticle diffusion occurs and the adsorption begins to happen on the inner channels and pores until the adsorbent is completely saturated with the adsorbate and equilibrium occurs (Albarelli, Rabelo, Santos, Beppu, & Meireles, 2011).

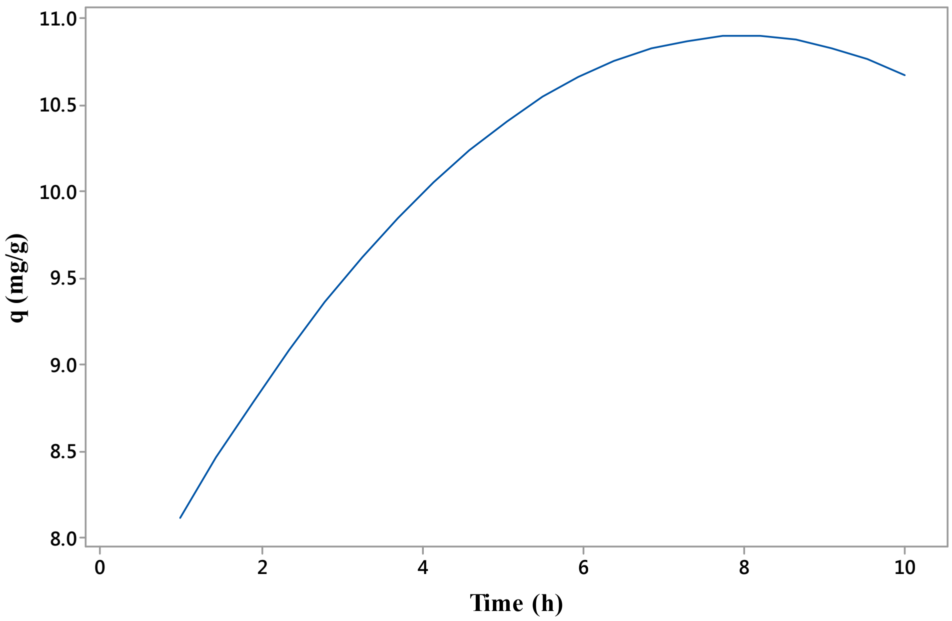

Figure 13: Effect of time on uptake for adsorbent dose 0.008 g mL, lead concentration 105 ppm for CO_2-DP

One of the main objectives of this study was to compare adsorption capacity of the three adsorbent types. The main research question was: does the extraction of lipids from date pit powder affect the adsorption capacity of the date pit powder? ANOVA results showed that the adsorbent type was no a significant factor on the response. The adsorbent type had a p-value of 0.056, which is just borderline insignificant, as factors with p-values less than 0.05 are considered significant. Figure 14 compares the average uptake (q) of each adsorbent. The mean adsorption capacity of S-DP, CO_2-DP, and R-DP were 10.87, 10.94, and 9.83 mg/g respectively. Both S-DP and CO_2-DP have displayed similar adsorption abilities, indicating that the type of extraction does not have an effect on the adsorption capacity. Both show higher adsorption ability than R-DP, suggesting that the extraction process does slightly increase the adsorption ability of date pit powder, but not to a statistically significant degree.

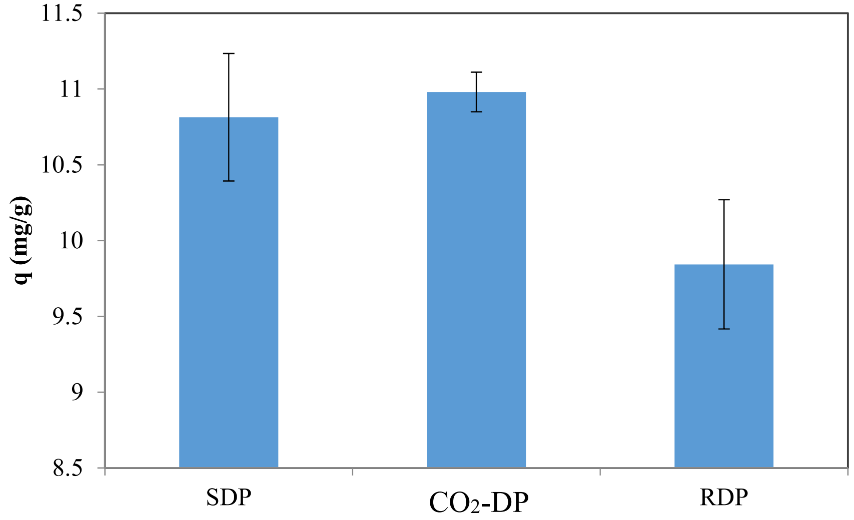

Figure 14: Comparison of adsorption capacity among adsorbent types for adsorbent dose 0.008 g/mL, lead concentration 105 ppm, and time 5.5 hours

3.3.3.3 Optimal Adsorption Conditions

In addition to producing a statistical model, Minitab was also used to find the optimal adsorption conditions. The optimization problem was solved for maximizing *q* and the solution is shown in Table 18. It was found that uptake was at its maximum (14.68 mg/g) when the adsorbent was CO_2-DP, dose was 0.0058 g/mL, lead concentration was 196 ppm, and time was 10 hours. These optimum values were based on a statistical analysis of experimental data collected.

Table 18: Solution of optimization of adsorption parameters

Solution	Dose (g/mL)	Pb concentration (ppm)	Time (h)	Adsorbent type	q Fit (mg/g)
	0.0058	196.16	10	CO_2DP	14.68

3.3.4 Adsorption Isotherms

The equilibrium data collected was fit to Langmuir and Fruendlich isotherms, equations (2) and (3) respectively mentioned in section 1.4.11. The equilibrium data is presented in Table 19, where c_e is the equilibrium lead concentration, and q_e is the equilibrium uptake. In Table 20, the values of the constants are presented as well as the correlation coefficients. The Fruendlich isotherm fits the experimental data better, as indicated by the R^2 value of 0.989 compared to 0.980 of Langmuir, although both give a satisfactory fit. Furthermore, the maximum adsorption given by the Langmuir model for CO_2-DP was found to be 31.39 mg/g. The Langmuir isotherm assumes monolayer adsorption on a homogeneous surface, and no interactions between the adsorbed ions. This suggests that adsorption uniformly increases with increasing concentration. The Fruendlich isotherm, however, is an empirical relationship which assumes adsorption on a heterogeneous surface (Al-Ghouti et al., 2010; Samra et al., 2014). Since both models give a satisfactory fit, it is suggested that both heterogeneous and homogenous monolayer adsorption occurs, as suggested by the Fruendlich and Langmuir models, respectively.

As shown in Figure 15, two lines are obtained for the Langmuir isotherm; one at low concentrations and one at high concentrations. This deviation from linearity is due to the way adsorption occurs on the sites. The adsorption sites have different binding energies, and the sites with the highest binding energies are filled first. Then when all of the monolayer sites have been occupied, the adsorbate is forced into the internal adsorption surfaces in the microspores and macrospores (Al-Ghouti et al., 2010; Allen, McKay, & Khader, 1989; Benjamin & Leckie, 1981; Khraisheh, Al-Ghouti, Allen, & Ahmad, 2004).

The results of this study are in accordance with other authors' findings for lead adsorption using various adsorbents. El-Naas et al. (2007) studied the adsorption of lead onto Chlorella vulgaris. To collect the equilibrium data, dose 2 g algae/L solution, 25°C, pH 5, lead concentration varied from 5-250 ppm, and shaking for 24 hours was used. The data was best fitted to Langmuir model ($R^2 = 0.9904$) with a q_m of 169 mg/g.In addition, Anantha and Kota (2016) studied the adsorption of lead by chicken feathers reinforced with chitosan. Equilibrium data was collected for adsorbent dose 6 g/L, and 20-100 ppm lead solution. Langmuir model was found to be the best fit model with q_m 70.42 mg/g. Furthermore, Samra et al. (2014) studied the use of waste raw date pits collected from Mansoura, Egypt for lead adsorption for lead concentrations 1-30 ppm and adsorbent dose 6 g/L. They found that both Langmuir ($R^2 = 1$) and Fruendlich isotherms were a good fit ($R^2 = 0.998$). The authors found the maximum uptake from the Langmuir model to be 2.891 mg/g, indicating that CO_2-DP in this study performed better. This could be due to differences in the nature of the date pit powder. Also in the experimental set up performed by Samra et al. (2014) the powdered date pits were dried for much less time than the date pits in this study. When adsorbents are not completely dry, remaining water molecules occupy some of the adsorption sites, leaving much less adsorption sites available for binding to lead. Also, Samra et al. (2014) studied much lower concentrations of lead than the concentrations of this study; therefore, their model and model parameters are limited by those concentrations. In addition the q_m of CO_2-DP of this study, 31.39 mg/g, was found to be similar to that of activated carbon (30.7 mg/g) and chemically modified activated carbon (30.6 mg/g) prepared from date pits by Abdulkarim and Al-Rub (2004).

Table 19: Adsorption equilibrium data

C_0 (ppm)	c_e	q_e
5.00	0.41	0.63
25.00	1.51	3.00
90.00	4.15	10.74
140.00	11.05	16.59

Table 20: Fitting of adsorption isotherm parameters.

Isotherm	Parameter	(value)
Langmuir	b (L/mg)	0.11
	q_m (mg/g)	31.39
	R^2	0.980
Fruendlich	K_F	3.23
	n ($1/b_f$)	1.44
	R^2	0.989

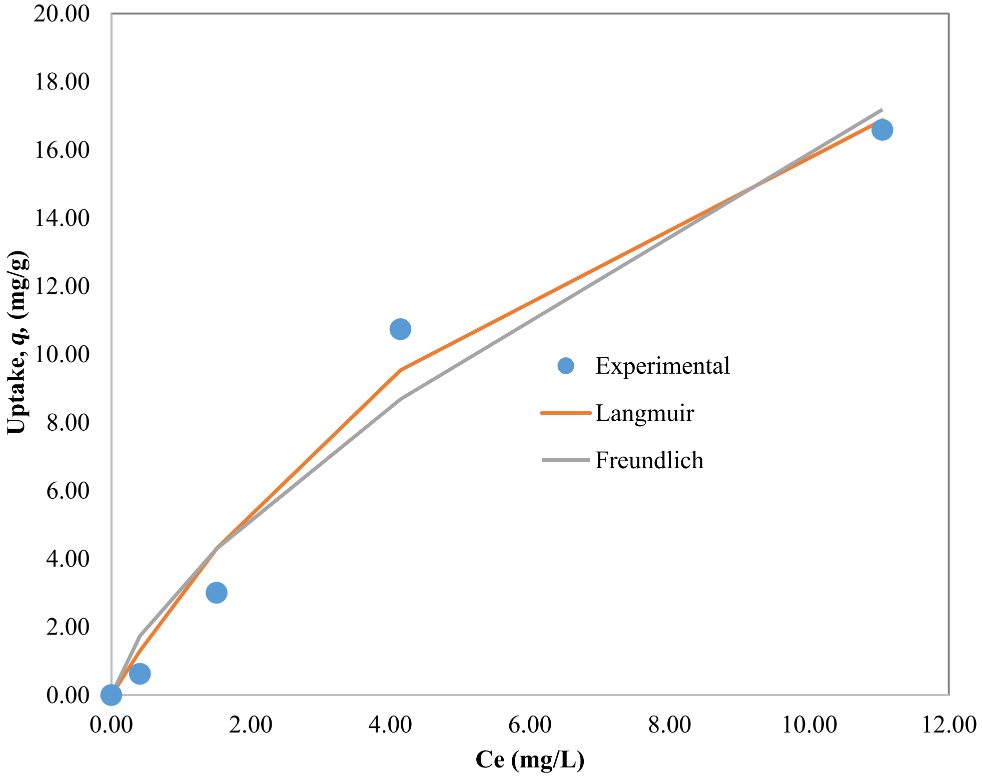

Figure 15: Adsorption isotherms

3.3.5 Characterization of Adsorbents

The adsorbent material that was subjected to various types of extraction experiments as well as the raw material were characterized using thermogravimetric analysis (TGA), infrared spectroscopy (IR), surface area and porosity analysis, and scanning electron microscopy (SEM). The results are discussed in the following sections.

3.3.5.1 TGA Analysis

TGA was carried out on samples of R-DP, CO_2-DP, and S-DP. The results are displayed in Figure 16. An initial thermal event occurs for all 3 powders at 100-150°C. This is related to the removal of physically adsorbed water. Its removal caused a 5% weight loss in the samples. In the case of raw date pits, another thermal event was observed at 250-300°C, which caused a weight loss of 60%. A third thermal event resulted in the complete combustion of the remaining solid material and continued until 675°C. This is also confirmed by the disappearance of the entire mass of the sample.

For S-DP and CO_2-DP a second event of weight loss was observed around 250-300°C, which resulted in an additional weight loss of 55% for both S-DP and CO_2-DP versus 60% of weight loss for the R-DP powder. This difference could be related to the partial removal of volatile oils from the date pit powder by the two methods described in this study. This was further confirmed by the presence of a third event of weight loss resulted in a sustained decomposition of the remaining material of the S-DP and CO_2-DP samples. In comparison with the burn out of remaining material of the untreated R-DP powder that was completed at 675°C, the S-DP and CO_2-DP remaining material were removed at 790°C. It should be noted that upon the completion of the TGA experiments, a black residue was observed after the TGA testing of the S-DP and CO_2-DP samples, but not for the raw date pits R-DP sample. Figure 17 shows a summary of the overall weight loss of the three samples, confirming this observation. These variations are attributed to the extracted oils from the RDP sample by Soxhlet and SC-CO_2 methods. The unburned mass of CO_2-DP sample was later analyzed by IR spectroscopy, as will be discussed in section 3.3.5.2.

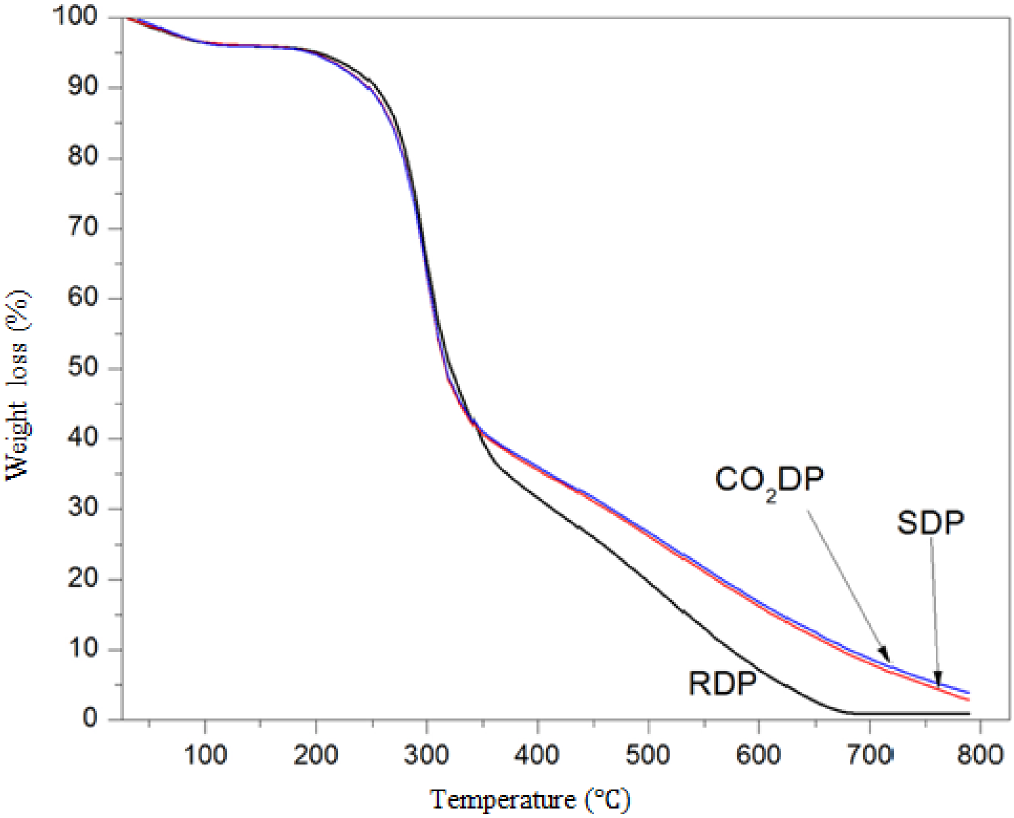

Figure 16: TGA analysis of adsorbent

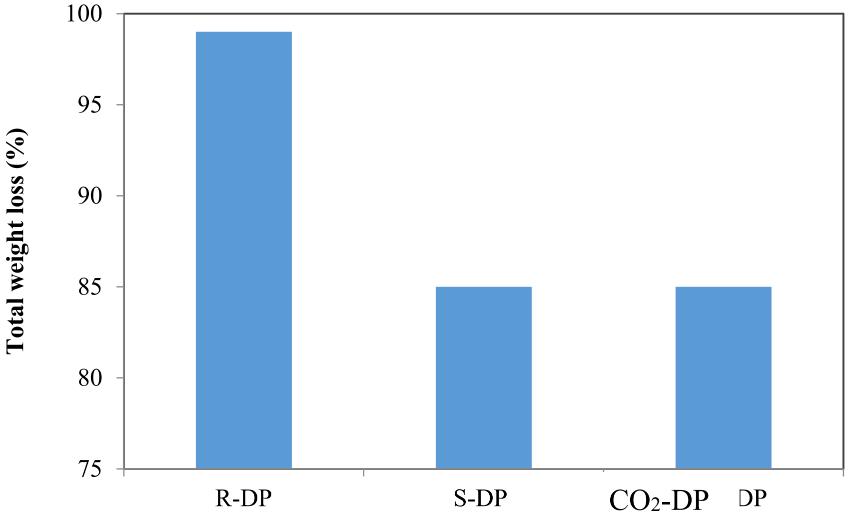

Figure 17: Comparison of weight loss for R-DP, S-DP, and CO_2-DP

Sait, Hussain, Salema, and Ani (2012) reported a weight loss of 5% in the range of 25-150℃ for a date pit sample, which was attributed to the removal of the water content of the sample. A similar weight loss was observed in Figure 16 for all three samples at 50-150℃. Sait et al. (2012) also reported a major weight loss at 308℃ which was attributed to the release of volatile matter. A similar thermal event can be seen in Figure 16 for all 3 adsorbents at 250-300℃. Sait et al. (2012) reported a proximate analysis for the date pit sample as follows: moisture 4.9%; volatile matter 76.6%; ash 10.8%; and fixed carbon 7.7%. The highest weight loss observed in all samples in the range of 250-300℃ is, therefore, attributed to the evaporation of the volatile matter, which was shown by Sait et al. (2012) to be the major component of date pit samples. Similar findings were reported by Babiker, Aziz, Heikal, and Yusup (2013) during their TGA analysis of 6 different types of date pit cultivars. According to these findings, Babiker et al. (2013) realized the detailed composition of date pits to contain lignocellulosic biomass that consists of hemicellulose, cellulose, and lignin. The chemical structure of these compounds are shown in Figure 20. Thermal decomposition of the lignocellulosic biomass occurs between 200-400℃, which can be observed as the sharp decrease in sample weight that occurs between 250-450℃ in Figure 16. In the low temperature range 160-360℃ hemicellulose decomposes. Cellulose decomposes at the higher range of 240-390℃ (Babiker et al., 2013). Furthermore, the pyrolysis of cellulose, hemicellulose, and lignin was separately investigated, where it was found that the weight loss of hemicellulose mainly occurred at 220-315°C, while that of cellulose occurred at 315–400°C, and that of lignin occurred at 160-900℃. The current results are, therefore, in accordance with the previous results of Sait et al. (2012) and Babiker et al. (2013).

3.3.5.2 IR Spectroscopy

Furthermore, IR investigation of composition was performed. This technique investigated the major functional groups of the spectroscopy is a technique used to identify the main functional groups present along the components of date pits. It was performed on R-DP, S-DP, CO_2-DP samples, as well as the unburned char that remained after performing TGA on CO_2-DP, which is labeled as CO_2-DP-A in Figure 19. The IR spectra of R-DP, S-DP, CO_2-DP are presented in Figure 18 and were used to identify the changes that occur in R-DP as a result of Soxhlet and supercritical carbon dioxide extraction processes. According to El-Hendawy (2006), the carbohydrate part of date pits consists mostly of cellulose, hemicellulose and lignin. The structure of these molecules are presented in Figure 20.

As shown in Figure 18, a broad band occurs between 3000-3700 cm^{-1} in all samples. This band is attributed to O-H and N-H stretching modes in the carbohydrate residues of the date pits. The broadness of this band was more pronounced in the IR spectra of R-DP and S-DP samples, while its broadness decreased in the IR spectrum of CO_2-DP sample. Functional groups containing N-H and O-H bonds are shown in the structure of cellulose; Figure 20 (El-Hendawy, 2006). The change in resolution of this band does not indicate the removal of these groups, but rather a refining of the cellulosic materials. Moreover, it should be mentioned that the O-H group is also attributed to the oily material that are contained in the raw date pits. Upon Soxhlet and SC-CO_2 extraction, these oils are removed, which is also an explanation for the decrease in intensity and broadness of this band in the IR spectra of S-DP and CO_2-DP samples. The difference in resolution among the spectra of S-DP and CO_2-DP also suggests that SC-CO_2 extraction was more selective than Soxhlet extraction. This conclusion is further supported by the difference in the fatty acid profiles among the oil samples collected by Soxhlet extraction and SC-CO_2 extraction, as shown in Table 12 in section 3.2.9.

Furthermore, the band at 1750-1760 cm^{-1} in Figure 18 is attributed to the C=O in the carboxylic groups of the oil. This band is apparent in the spectrum of R-DP, however it greatly decreased in intensity in the spectra of CO_2-DP and S-DP to the point where it is only a shoulder. This is clear evidence of the removal of these oils through SC-CO_2 and Soxhlet extraction processes. On the other hand, Briones, Serrano, Younes, Mondragon, and Labidi (2011) reported a band at 1730 cm^{-1} for raw date pits, which was attributed to C=O stretching in hemicellulose. However, this is not supported by the current results. As shown in Figure 18, the band in the range 1750-1760 cm^{-1} is attributed to the C=O in the carboxylic groups of the oil, and it is clear that is the component which has been removed during extraction. There is further evidence of the removal of fatty acids from the GC chromatography, as discussed in section 3.2.9. On the other hand, the band at 1630 cm^{-1} in Figure 18 is attributed to NH_2 bending of amines, whereas the band at 1520-1530 cm^{-1} is attributed to aromatic ring stretching, and is supported by the findings of Sait et al. (2012). These bands were not affected by extraction.

The IR spectra of R-DP, S-DP, and CO_2-DP have given evidence of the removal of oil from date pits as a result of the Soxhlet and SC-CO_2 extraction processes. This is further supported by the GC analysis of the fatty acid profiles of oil samples taken from each extraction process. The IR spectra gave a more comprehensive understanding of the groups that the adsorbents are composed of. They illustrated the differences that the extraction process makes, which is the removal of oils that contain carboxylic acid groups. The statistical analysis presented in 3.3.3.2 shows that there is no significant difference in the adsorption capacity of the three adsorbents studied. This indicates that the removal of oil does not significantly affect the adsorption capacity. However the continued broadness in the spectrum of S-DP at 3000-3500 cm^{-1} indicates a lower extent of extraction of organics when using Soxhlet extraction, compared to SC-CO_2 extraction. These results further suggest that SC-CO_2 extraction is more selective than Soxhlet extraction in extracting organics.

Figure 19 shows the IR spectrum of the remains of the TGA analysis of the CO_2-DP (CO_2-DP-A) sample. A high intensity band was observed at 1000 cm^{-1}, which was also observed in the IR spectra of other samples. The presence of this band and the continued presence of a band at 3400-3500 cm^{-1} was not previously shown in the literature to the best of the knowledge of the author. The DP sample that was subjected to SC-CO_2 showed an incomplete combustion, and this was reflected in the presence of bands in the IR spectrum of the remains of the sample that was heat treated during its TGA analysis up to 800℃. These findings may indicate the presence of a thermally stable material due to the effect of SC-CO_2 extraction procedure. The absence of O-H and C=O bands in the IR spectrum of this sample may indicate the presence of amine-based residue in the remains of the CO_2-DP sample, where the band at 3400-3500 cm^{-1} and the band at 1000 cm^{-1} are related to the stretching and bending modes of N-H bond, respectively.

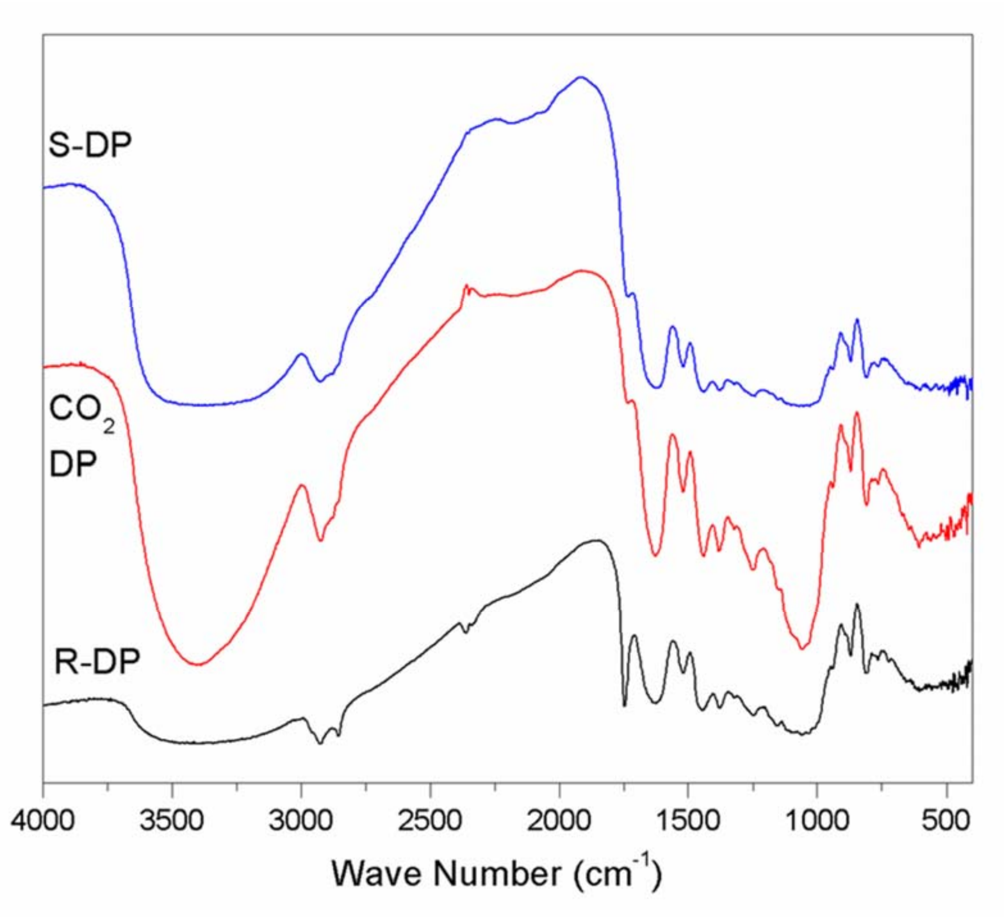

Figure 18: IR spectra for adsorbents R-DP, S-DP, and CO_2-DP

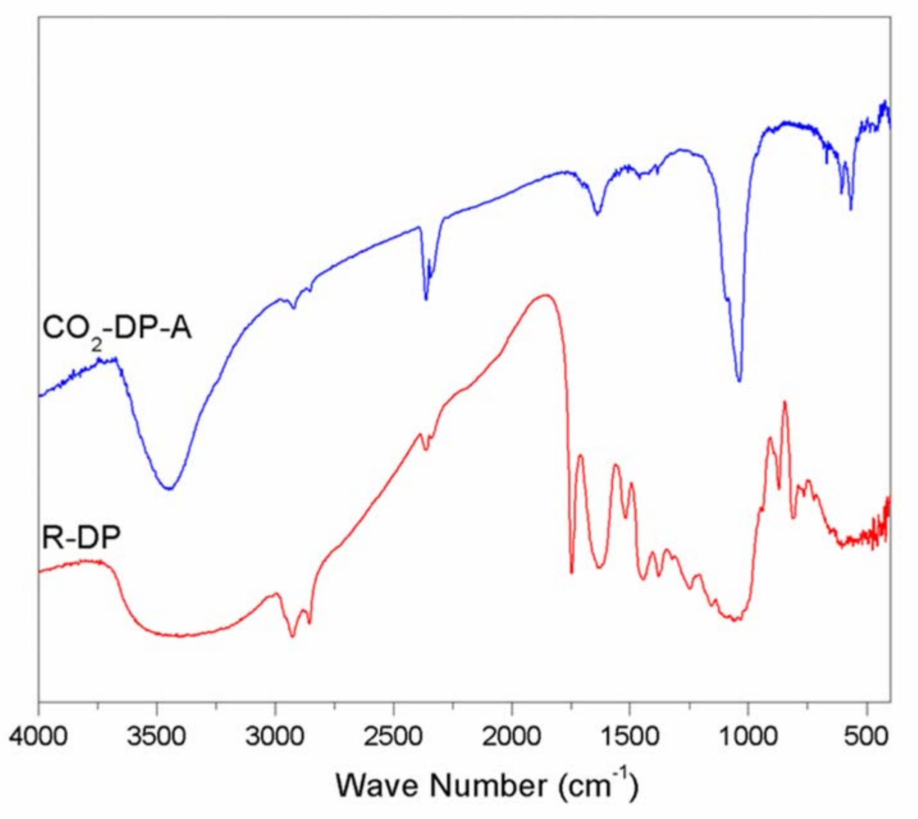

Figure 19: IR spectrum of R-DP and CO$_2$-DP-A

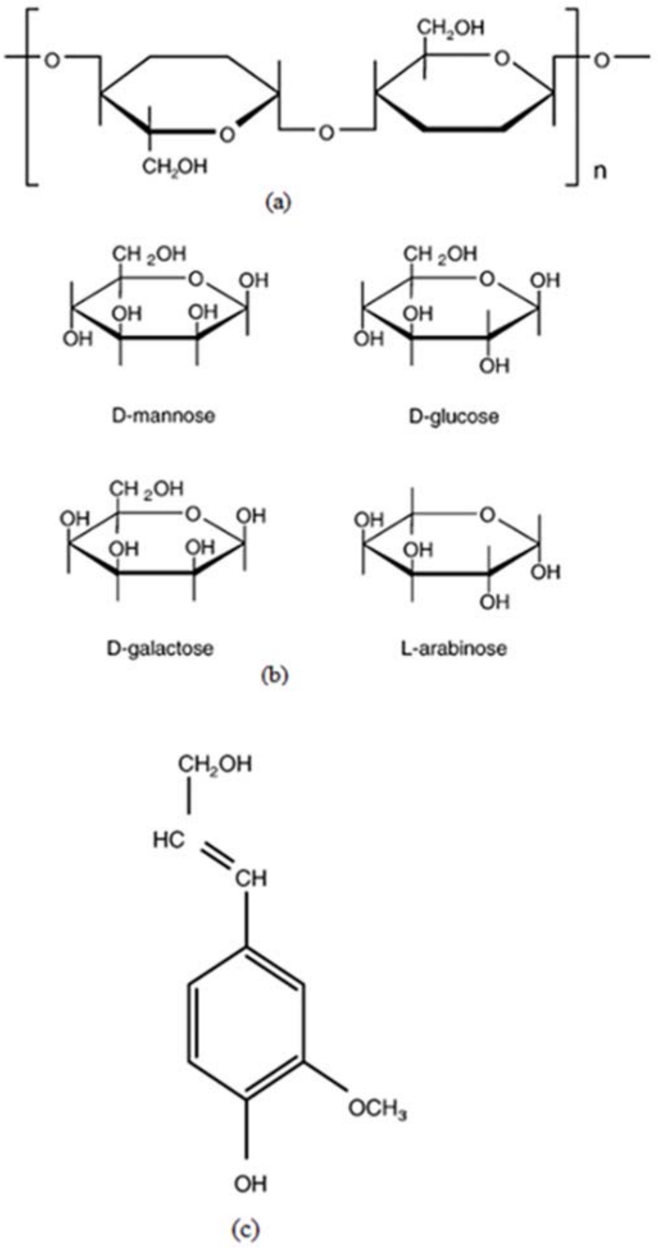

Figure 20: (a) Cellulose molecule, (b) principal sugar residues of hemicellulose, and (c) phenylpropanoid units found in lignin

3.3.5.3 Surface Area and Porosity Analysis

N_2 adsorption was used to analyze the surface area and porosity. Figure 21 shows N_2 adsorption isotherms of the R-DP, S-DP and CO_2-DP dried powders. While R-DP showed a minor adsorption of N_2 gas onto and into its porosity, the S-

DP and CO_2-DP powders showed a higher extent of adsorption. Both S-DP and CO_2-DP showed type II isotherm, as compared with Figure 22 (Rouquerol, Rouquerol, & Sing, 1999) that shows the types of adsorption isotherms. It should be noted that the S-DP powder sample showed a slightly higher extent of N_2 adsorption than the CO_2-DP powder sample. These results indicate the formation of porosities upon the removal of the oils from the R-DP powder using both Soxhlet and SC-CO_2 methods of extraction, with the S-DP showing a higher degree of porosity. Figure 23 compares the effect of porosity development on the BET surface area of the powders as compared with that of the R-DP sample. The relatively low volume of N_2 adsorbed on the S-DP and CO_2-DP powders was reflected in low values of surface area of 0.92 and 1.2 m^2/g, respectively. In contrast, the R-DP powder did not show a significant value of a surface area, which is attributed to the non-existence of porosity in the raw powders.

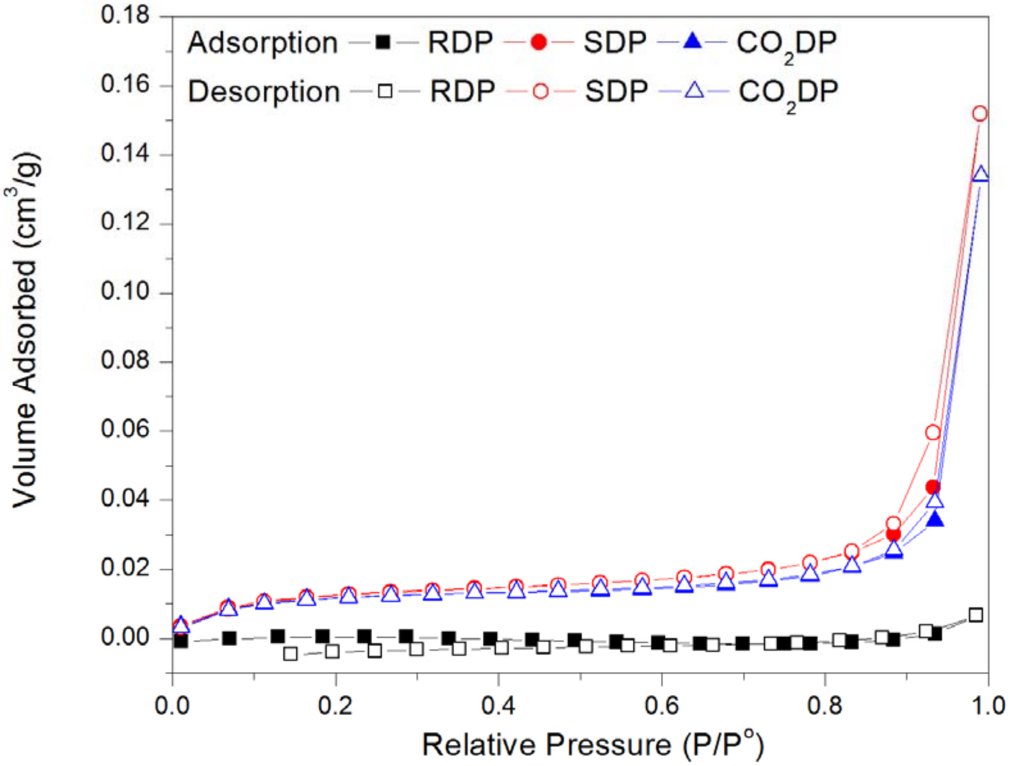

Figure 21: N_2 adsorption isotherms R-DP, S-DP and CO_2-DP

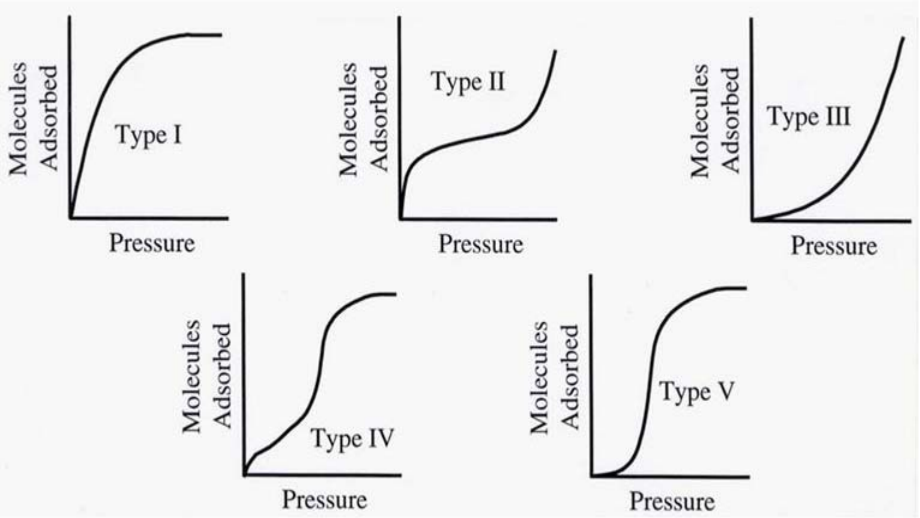

Figure 22: Types of adsorption isotherms

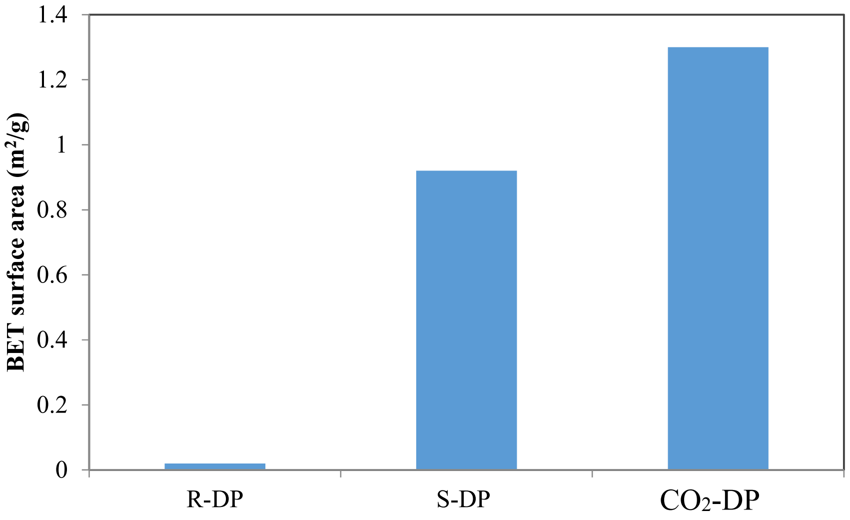

Figure 23: Comparison of surface areas of R-DP, S-DP and CO_2-DP samples

3.3.5.4 SEM

Figure 24 shows SEM micrographs of the R-DP, S-DP and CO_2-DP solid powders. All powder samples showed a variable distribution of irregular shape particles. However, the presence of soft edges and agglomerates in the R-DP micrograph is related to the presence of organic materials, mainly oils, in the powder. In contrast, the refined aggregates with sharp edges in the micrographs of the S-DP and CO_2-DP samples indicate the removal of the oily surface coverage from the surfaces of the solid particulates. In addition, it can also be noticed that the presence of an oily layer aggregating the solid particulates of the R-DP powder explains the low porosity and reduced surface area of the untreated powder. On the other hand, the removal of the oily layer in the S-DP and CO_2-DP samples resulted in a decrease in the extent of agglomeration of the solid particulates and the exposure of surfaces and porosities, which in turn explain their relatively higher N_2 adsorption and surface area.

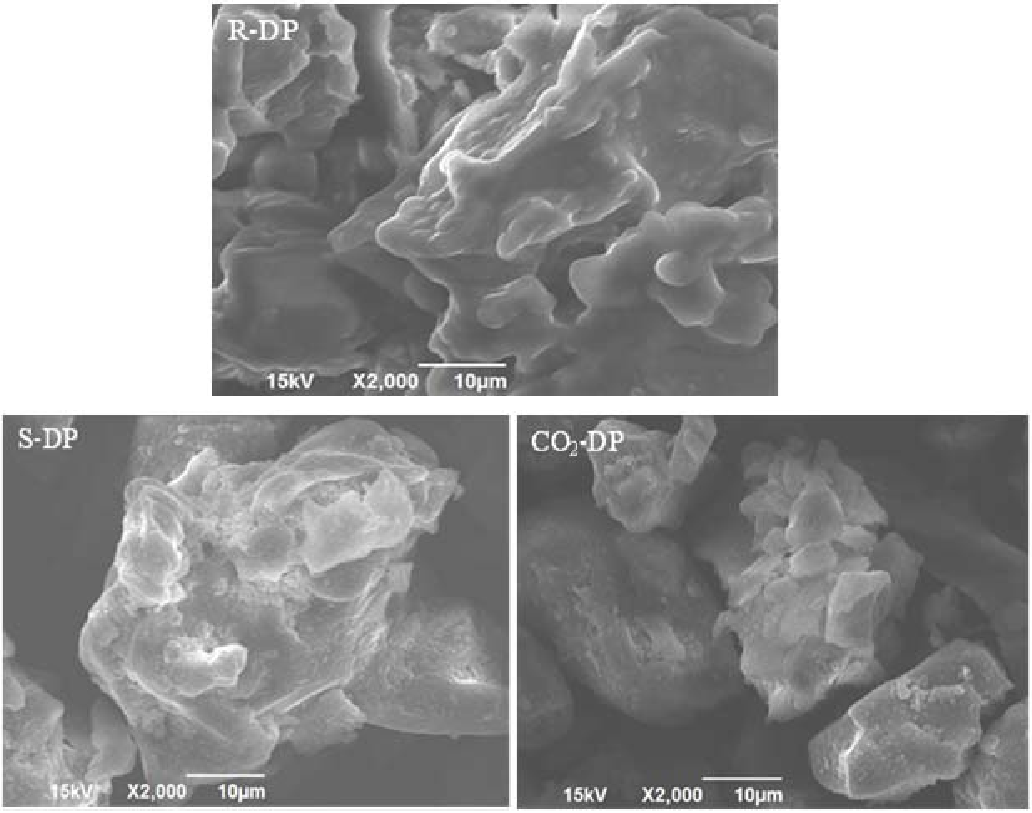

Figure 24: SEM images of R-DP, S-DP and CO_2-DP at magnification 2000

Chapter 4: Conclusion

In this study, waste Khalas date pit powder was subjected to Soxhlet and supercritical carbon dioxide extraction to obtain date pit oil. The residue powders of the extraction processes and raw date pit powder were then investigated as adsorbents for the removal of lead from solution.

Supercritical carbon dioxide extraction was found to be an effective method for extracting oil from date pits. The effect of pressure, temperature, and particle size on the yield were studied, and pressure was found to be the only significant factor. The optimal extraction conditions were found to be 500 bar, 40℃, and <63 µm. At the optimal value, supercritical carbon dioxide extraction gave the same yield (10.29%) as Soxhlet extraction (10.3%), indicating that it can be used as an alternative extraction method. In addition, the fatty acid profile of oil extracted by SC-CO_2 differed slightly from that of oil obtained by Soxhlet extraction, indicating that SC-CO_2 is more selective to certain components.

Furthermore, the powder residues from the extraction processes and raw date pit powder were shown to be effective adsorbents for the removal of lead. The extraction of oil did not have a significant effect on the adsorption capacity of the adsorbents. The optimum adsorption conditions were dose 0.008 g/mL solution, lead concentration 196 ppm, time 10 hours, and adsorbent type CO_2-DP.

TGA and IR characterization of the adsorbents showed that organic compounds had been extracted. This was apparent in the reduction of the thermal events in the TGA of S-DP and CO_2-DP compared to R-DP, and in the shrinkage of the band attributed to carboxylic groups in the IR spectra of S-DP and CO_2-DP compared to R-DP. Furthermore, the IR spectra suggest a lower extent of extraction of organics when using Soxhlet extraction, compared to SC-CO_2 extraction; indicating that SC-CO_2 extraction is more selective toward certain organics than Soxhlet extraction.

In addition, the surface area and porosity of the adsorbents increased as a result of the extraction process. This is true for both Soxhlet and SC-CO_2 extraction. SEM images also confirmed the exposure of new surfaces and the creation of more adsorption sites as a result of extraction. This helps explain why the adsorption capacity of S-DP and CO_2-DP was slightly higher than that of R-DP, though not a statistically significant degree.

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