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Research Article

Supercritical Extraction and Modeling of Citrullus Colocynthis Plant Using Carbon Dioxide

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ABSTRACT:
Citrullus Colocynthis is a herbal plant with rich content of phytochemicals. This old plant in Iran have been used for Diabetic disease. This research, the supercritical fluid extraction (SFE) with carbon dioxide (CO2) and Ethanol (Etoh) as co-solvent was applied to obtain the yield and the combination of components. Then Citrullus Colocynthis, is essential oil was analyzed by GC-MS tests. The extraction was explored at various operating condition using 150,170,190 bar and 35, 40, 45 ˚c.With comparison of all of these operation condition results, the bestoperation condition was obtained in 190 bar and 45 ˚c.The yield in this situation was 26.576. and the constituents were identified and divided into five classes include: alcohols,alkanes,hydrocarbons,esters and acids.1,2-benzenedicarboxylicacid, mono(2-ethylhexyl)ester,4-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester , Phthalic acid, 6-ethyloct-3-yl 2-ethylhexyl ester , and n-hexadecanoic acid'small scale model was used to extraction process modeling. This model based on the mass balanceto connects with the experimental data isused. Three parameters of model are the molecular diffusion coefficient (D_{AB}), mass transfer coefficient (k_f) and axial dispersion coefficient (Dax). Model used to fit well with experimental data and this show compliance with the supercritical extraction systemis studied here. The oil with gas chromatography (GC) and mass spectrometry (GC-MS) were analyzed. Then the examined of extraction products by GC and GC –MS

Keywords: Citrullus Colocynthis, supercritical extraction, carbon dioxide, essential oil

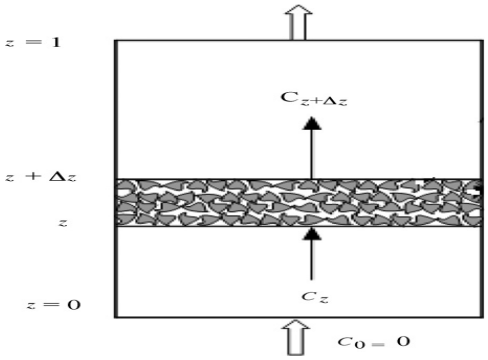
INTRODUCTION

Essential oil from plants has been used as Herbal Medicine and incense since ancient times. Citrullus colocynthis (L.) Schrader (cucurbitaceae family) is a fruit commonly known as bitter apple or bitter cucumber, found in Sudan, Iran and India. Colocynth is widely used in folk medicine since centuries. The interest in its anti-inflammatory properties has been renewed in modern times. Conventionally Citrullus colocynthis fruits are used in antidiabetic treatment in Mediterranean countries. The seed extract induce insulin secretion and that this could at least partially account for the antidiabetic activity of these fruits. [1] Earlier, the antioxidant effects and the effect of the aqueous extract of the pulp on kidney and liver functions were reported.[2] The leaves of Citrullus colocynthis showed significant antimicrobial, antidiabetic, antioxidant, local anesthetic, and anti-inflammatory activity reported.[3] Cucurbitacin glucosides seem that could become important for the therapy against breast cancer cells because of its ability to modify cell morphology and

signaling as well as to induce apoptosis and changes in mitochondrial membrane potential.[4] Citrulluscolocynthis oil possesses the delicate aroma of the spice and pungent taste. Aromas present in food samples belong to different chemical families, including esters, ketones, aldehydes, alcohols, terpensphenols and its derivatives. It is employed mainly in the flavoring industry [5].The supercritical extraction from the Citrulluscolocynthis has not been reported to date. The aim of this work was to extract compounds from it and fine the best operation condition for industrial application.

Mathematical modeling:

Sincethe obtain of experimental data at high pressures is difficult and the other side testing in all of temperatures and pressure condition are very costly, expansion and modification of existing models to fit the experimental data are very useful for a supercritical fluid system. For modeling consider the tank extractor cylindricaly. Due to the cylindrical feed chamber, elements for the study of mass transfer in fluid as follows:



The gas phase equation is obtained is:

$$\frac{\partial C}{\partial t}+V\frac{\partial C}{\partial z}-D_{ax}\frac{\partial^2 C}{\partial z^2}+\frac{1-\varepsilon}{\varepsilon}\frac{\rho_s}{\rho_f}\frac{\partial q}{\partial t}=0 \quad (1\text{-}1)$$

And the solid equation is:

$$\frac{R_p}{3k_f}\frac{\rho_s}{\rho_f}\frac{dq}{dt}=(C-C_s) \quad (1\text{-}2)$$

By definition dimensionless numbers Bi and Penumberas follows:

$$Pe_P=\frac{R_p V}{D_{ax}} \quad (1\text{-}3)$$

$$Bi=\frac{R_p k_f}{D_{ax}} \quad (1\text{-}4)$$

Finally we get to the following equation:

$$\frac{\partial C}{\partial t}+\frac{\partial C}{\partial z}-\frac{1}{Pe_p}\frac{\partial^2 C}{\partial z^2}-\frac{1-\varepsilon}{\varepsilon}\frac{3L}{R_p}\frac{Bi}{Pe_p}(C-C_S)=0 \quad (1\text{-}5)$$

$$\varepsilon=1-\frac{\rho_a}{\rho_p} \quad (1\text{-}6)\ \&\ (1\text{-}7)$$

$$\rho_a=\frac{m}{v}$$

m:Mass of plant (gr)

v:the volume of cell (cm^3)

ρ_p:Density of particle (gr/cm^3)

Experimental:

The fruits of Citrullus colocynthis was collected in july 2015 in the region of the plains of kazeroon in iran (lat.29˚27′N;long.51˚39′15″E). Harvested material was dried in the air, protected against direct sunlight, until a constant weight was achieved. The raw fruits of Citrullus colocynthis kept at favourable temperature(25-30˚C) for ripening. The Citrullus colocynthis pulp and leaves were milled in a blender for 60 seconds and then sieved and subjected to sc-CO2 extraction. Dichloromethaneand ethanol was obtained from Merck. The efficiency of the different extraction processes is assessed using the extraction yield, defined as the mass of plant before test minus the mass of plant after test divided by initial mass of the raw plant.we can say Briefly, this apparatus is composed of a 113 mL (16 cm height and 3 cm internal diameter) tubular extractor (200 bar max) with a cascade of three 15-mL cyclonic separators connected to the extractor outlet. The system was operated at a temperature between 35 and 45◦C and pressure of 150 and 190 bar for volatile fraction extraction. Pure CO2 was passed into the cell in all runs.theexperiment consisted of two stages.The first step is performed in a static state that the output valve is closed and the gas is in direct contact with sample.It took about 30 minutes.after the static time we slowly open the outlet valve.during this time must be taken that

the temperature and pressure does not change.After this dynamic period begins that starts from when the valve opened and lasts about an hour

RESULTS AND DISCUSSION:

In the first experiment that done at 45˚c and 190 bar are measured 5.0120 grams of raw plantand then the raw plant was put into the cell.Cell weight beforeand after the test comes 25.5687, 25.4355.so According to the above equation we can obtain yeild=2.6576.in the following tablethe Efficiency have been calculated for other temperatures and pressures.

Table 1. Supercritical extraction efficiency at different temperatures and pressuresin Citrullus colocynthis essential oil.

No.	Pressure	Temp ^{0}C	Yield
1	190	45	2.6576
2	190	40	2.217
3	190	35	2.027
4	170	45	1.348
5	170	40	1.195
6	170	35	1.141
7	150	35	0.5623
8	150	45	1.005
9	150	40	0.7821

To measure the amount of C. colocynthis oil, the dried C. colocynthis kernel became powder by an electric mill and extraction was done by supercritical method and solvent of Dichloromethane. To analyze of samples the Helium's gas chromatography method was used. Oven program: initial temperature: 40◦C for 3 min, 40◦C to 200◦C at 7◦C.min-1, 200◦C to 290◦C at 40◦C.min-1 and the final temperature is kept for 8 minutes.From the before experiment the highest Efficiency obtained in the operating conditions at 190 bar and 45˚c.

At this condition we do the GC-MS analysis.The resulting compounds are noted in the table below.

Table 2. Compounds obtained from GC-MS analysis of supercritical extraction from C.colocynthis essential oil.

Chemical composition	Molecular Formula	Area %
Benzoic acid, 2-ethylhexyl ester	$C_{15}H_{22}O_3$	0.28
n-Hexadecanoic acid	$C_{16}H_{32}O_2$	3.03
Octadecanoic acid	$C_{18}H_{36}O_2$	0.62
Tetradecanoic acid	$C_{14}H_{28}O_2$	1.08
Octadec-9-enoic acid	$C_{18}H_{34}O_2$	1.29
1,2-Benzenedicarboxylic acid, bis(2-methoxyethyl)	$C_8H_6O_4$	0.74
Phthalic acid, isobutyl octadecyl ester	$C_{30}H_{50}O_4$	0.42
Heneicosane	$C_{21}H_{44}$	0.14
Eicosane	$C_{20}H_{42}$	0.31
Benzamide	C_7H_7NO	0.75
1,4-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester	$C_{24}H_{38}O_4$	6.65
Phthalic acid, 6-ethyloct-3-yl 2-ethylhexyl ester	$C_{26}H_{42}O_4$	5.32
1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl)ester	$C_{16}H_{22}O_4$	73.16
1,2-Benzenedicarboxylic acid, ditridecyl ester	$C_{34}H_{58}O_4$	0.24
2-Pyridinecarbohydrazonamide	$C_6H_8N_4$	0.44
Squalene	C_3H_{50}	0.36
Docosane	$C_{22}H_{46}$	0.86
Nonacosane	$C_{29}H_{60}$	0.68
Tert-Butyl-p-benzoquinone	$C_{10}H_{12}O_2$	0.49
Tridecane	$C_{13}H_{28}$	0.61
Tetradecane	$C_{14}H_{30}$	0.85
Pentadecane	$C_{15}H_{32}$	0.85
Hexadecane	$C_{16}H_{34}$	0.61
Octadecane	$C_{18}H_{38}$	0.76

At a temperature of 318 ° K and the pressure of 190 bar we obtained the maximum yield. In this condition at 5 different times achieved the rate of yield with testing in laboratory and then compared it with the value calculated from the mathematical model with using matlab program. The bottom graphas wellshow it.Ascan be observedthe experimental datais matchwithmathematical modeling.

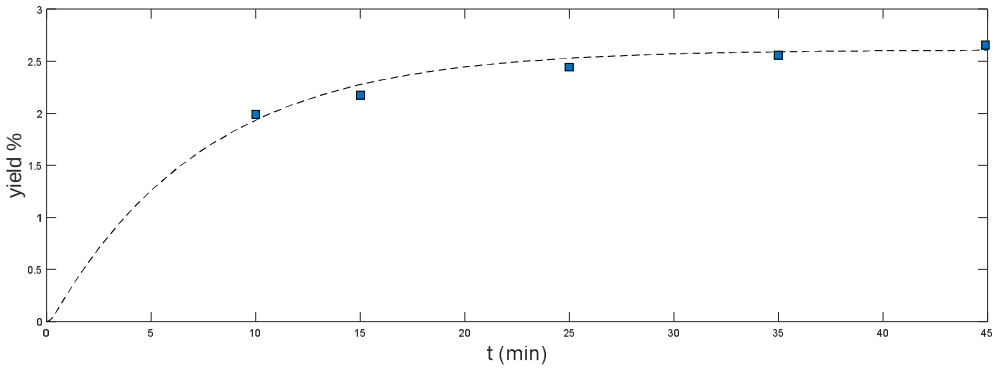


Fig 1-Compare the extraction efficiency of laboratory method and mathematical modeling

To measure the absolute error of the following formula is used:

$$AARD=\frac{1}{n}\left|\sum\frac{Y_{experimental}-Y_{calculate}}{Y_{experimental}}\right|\times 100=$$

$$\frac{1}{5}\left(\left|\frac{(2.04-1.95)}{2.04}\right|+\left|\frac{1.28-1.15}{1.28}\right|+\left|\frac{1.39-1.45}{1.39}\right|+\left|\frac{1.51-1.57}{1.51}\right|+\left|\frac{1.66-1.59}{1.66}\right|\right)=0.0299\times 100=3\%$$

The measurement error indicates the harmony of mathematical models with experimental data.As already noted, the test were performed at 3 pressure and 3 different temperature. Now compare the yield at different pressure that obtained through tests in laboratory with the predicted value of the mathematical model to understand the modelerror. The temperature is 318 kelvin and is constant. As It is known from the graph with the increased pressure also increases the extraction yield.in act with Rising pressure from 150 to 170 bar the yield convert from 1.0058 to 1.34 and in above pressure in 170 bar the yield is 2.6576.

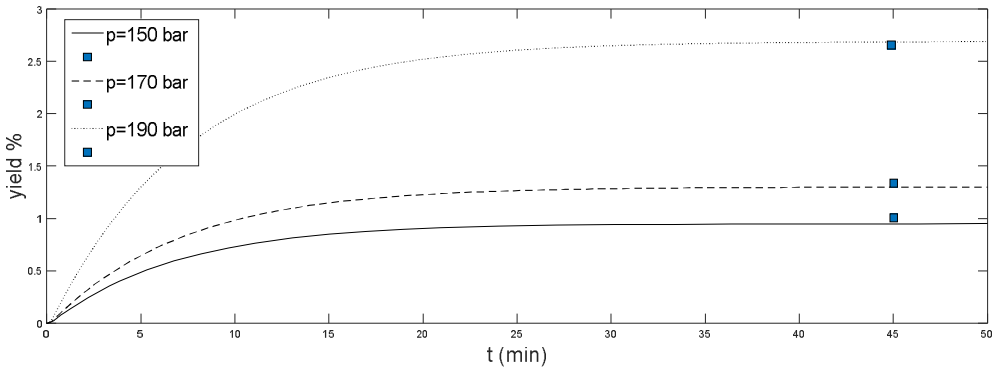


Fig 2-The extraction efficiency at different pressures

Now we examine the efficacy of thetemperatureontheextraction. To do this we obtained extraction efficiency at three different temperatures in constant pressure. The constant pressure was 190bar. The effect of temperature on the extraction can be both a positive and negative effect. This means that at temperatures between 30 and 50°Cincrease in temperaturethe desired effecton theextractof the plant, but at temperatures above50°Cincrease in temperaturewill havean adverse effect ontheextraction.in this tests

with the incrementof temperature from 308 to 313 kelvin the yield become more from 2.027 to 2.217.if the temperature be 318 kelvin the yield is 2.6576. However,asnotedbya highertemperatureof323° Ktemperature increaseis notthe desired effect.

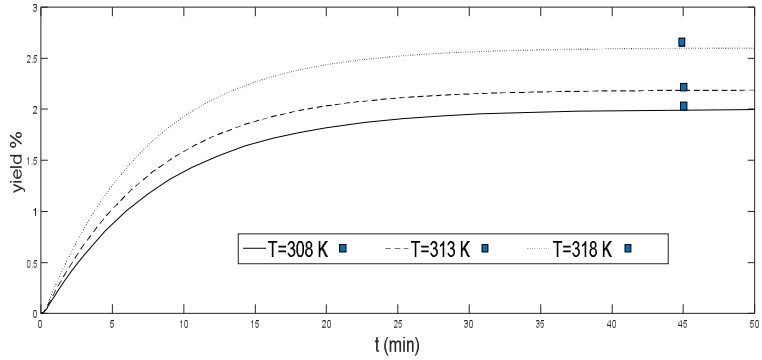


Fig 3-The extraction efficiency at different temperatures.

CONCLUSION:

As was observed at temperature 45 ˚ C and a pressure of 190 bar achieved the highest efficiency.Thus increasing the pressure and temperature desired effect on the Citrullus colocynthis plant. At this temperature and pressure, maximum yield obtained 2.6576. the constituents were indentified and divided into five classes include; alcohols, alkanes, hydrocarbons, esters and acids. 1,2-benzenedicarboxylic acid, mono(2-ethylhexyl)ester 73%,1,4-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester 6.65%, Phthalic acid, 6-ethyloct-3-yl 2-ethylhexyl ester 5.32%,and n-hexadecanoic acid 3.03%.As we have seen in the graph،model predicts that the extraction rate increases with increasing pressure that suggest with the results of the Experiments. With increasingpressure,densityandviscosity of thefluidincreases, but the impact of thisis more to increasethe density of thefluidand thereforewith increase of pressurethe Sherwood numberincreases andwhen increasemass transfer coefficient, the efficiency ofextractioncan be increased.also we know from the graph that that themathematical modelis consistentwithexperimental dataanalysis.We can alsosayabout the effects oftemperature that increase in temperaturewill reduceviscosityand decreasedensity, and these two parametersareinfluentialin determining thevalue ofSherwood,Butviscosityreductionismore from the reduce of density.As a result, the numerical value of the Re and Sc and thus the amount of Sherwood increases. This is cause to increases themass transfer coefficient (Kf).As a result, the efficiency predicted by the model increases with the TemperatureRising.

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