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Original Article

Overcoming challenges in cold press aided extraction of orange peel oil

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ABSTRACT

The use of cold press (CP) for recovery of orange essential oil from orange peels has limitation due to poor oil yield and merging CP with conventional solvent or high temperature distillation affects the oil quality and hence it is important to enhance the CP oil yield retaining the quality of oil. In the present work the parameters for CP including the effect of *albedo*, orange peel average particle size, physical and chemical properties of the aqueous phase obtained after CP are examined which explains the reason for the poor oil yield by CP. Also, a green aqueous extraction (AE) process that eliminates the use of solvent or enzymes or high temperature and time has been designed. The developed CP produced ~0.12 g of oil at 0.75 h, CPAE produced ~0.79 g of oil at 2.25 h which can be an alternative to the available orange oil extraction methods.

Keywords: Mechanical press, Essential Oil, Green Extraction, oil- water emulsion, solvent-free, *Citrus sinensis*

INTRODUCTION

There is huge production of orange fruit world-wide[1]. The fruit juice processing industries subjects the peels to cold press to extract oil. The mechanical press enables extraction of superior quality orange peel oil as it causes compression and rupture of the plant cells which expels the cellular components, without any chemicals or heat. The mechanical press used for oil extraction are mainly of two types. The first type of machine works on pressure generation (FMC 'In-line' rotary extractor and Sfumatrice extractors). The second type works on the principle of abrasion (Brown peel shaver, Pelatrice, and Raspadoras extractors) [2]. Depending on the design of the press, a solid cake of the peel residue (30-50 % w/w) and the liquid phase 50- 70 % w/w moisture content, is expelled out from the peels and drained through a perforated plate. The liquid so drained out is usually an emulsion of the oil in aqueous phase [3]. Thus, the cold press process is reported to give about 0.3 % w/w of oil from the peels. Solvent treatment with n-hexane or n-propanolol is usually reported after the cold press treatment to further extract remaining oil from the peel residue and/or the

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emulsions [4]. The solvent treatment, steam distillation temperatures affects the quality of oil and enzyme treatment is cost intensive [3-4]. There is a need for intensifying the cold-press process and recover the orange oil from the peels effectively without affecting the quality of the oil.

Olaniyan and Yusuf [6] reported cold press pre-treatment followed aqueous cooking for oil extraction from the groundnut. A similar process, if developed for orange oil extraction, can be constructive as the process will avoid use of any solvent, and will not require high temperatures for distillation of solvent from oil.

Upadhay et al [7], and Orsat Routry, [8] have reported that exposure to microwaves (MW) enhances the extraction of active ingredients from plant materials into the extracting medium[6-7]. This happens by rupturing the cell wall of the plant material by pressure created by the vaporised water due to heating caused by microwaves.

In the present work, the challenge of emulsion formation upon cold press treatment of fresh orange peel for oil extraction is elucidated and is resolved by a green solvent-free method of aqueous extraction of direct cold pressed orange peels and microwave aided cold pressed orange peels at milder temperatures than that used for distillation.

MATERIALS AND METHOD

Materials: Fresh orange peels were collected from the local fruit juice processors.

Equipment's for Extraction: Mixer with coarse and fine blade produced an average particle size of 1.6 mm and 0.2 mm. A stainless steel screw press/ cold press of height 0.08 m and diameter 0.04 cm was fixed with screws on a stable platform to enable efficient extraction of oil. The cold press had a removable sieve plate at the base with of pore size 0.5 mm for expelling of the aqueous phase.

A Samsung MW oven (Model No. S100) was used to perform the MW pre-treatment and was accompanied by a condenser at the top with cold water circulation. A 250 cm^3 capacity baffled glass reactor (0.07 m diameter: base, 0.18 m height) equipped with an overhead stirrer and turbine impeller (0.02 m diameter of pitch blades) was employed to conduct the aqueous extraction. The oil that surfaced on the perforated plate of cold press equipment was aspirated using a micro-pipette.

Equipment's Characterization: A Beckman coutler counter was used for determination of peel particle size. The physical properties of the aqueous phase were determined to get better knowledge about the emulsion. The density of the aqueous phase was measured after the cold press process using the Anton Paar densitometer (DMA 4500).The emulsion was characterised for the size of oil droplets using a Olympus BX-51microscope equipped with DP20 3.2 Mega pixel camera and a stage micrometer. The surface tensiometer (Komal Scientific Ltd.), pH and conductivity meter (Thermo Scientific) were used for the determination of the surface tension, viscosity, pH, conductivity of the emulsion. The electrophoresis apparatus having DC power supply with cathode and anode of aluminium was used for determination of charge on the oil droplet present in the emulsion. A high speed centrifuge (Beckman) was used to separate oil from aqueous emulsion obtained after-cold press method.

CHARACTERIZATION OF OIL

The organoleptic tests were used to characterize the extracted oil, the oil was then characterized both quantitatively and qualitatively by gas chromatography-Flame ionization detector- mass spectrometry (GC-FID-MS) and high performance liquid chromatography- photodiode array detector-mass spectrometry (HPLC-PDA-MS). The GC-MS analysis was performed using Thermo Scientific Co. equipment, BP-1 coloumn, with injector and detector temperatures at 240 ^{0}C, the heating ramp rate of oven at 12 $^0C.min^{-1}$ upto 210 ^{0}C and at 55 ^{0}C cooling temperature. The HPLC-MS was performed using Thermoelectron corp. Finnigam LCQ advantage Max equipment, with C-18 column, 50: 50 acetonitrile and methanol mixture as mobile phase at a flow rate of 0.3 cm^3min^{-1}.

EXPERIMENTAL METHODS

Optimization for Extraction of Orange Peel Oil by Cold Press (CP): At a time, 100 g of *albedo* free orange peels of 0.2 mm average particle size were compressed in the cold press machine to recover maximum amount of aqueous emulsion and a compressed solid peel residue. The compressed residue was collected and subjected to re-compression until the traces of liquid was collected. The number cold-press cycles were optimized to recover the maximum amount of emulsion and a dense dry cake of peel residue. The cold press process was optimized for the effect of average peel particle size (using peels with only *flavedo*) of 0.16 mm, 2 mm, and 1x 1 cm and for the effect of *albedo* (using peels with particle size 2 mm). Subsequently, the dry residue obtained from cold press extraction was subjected to hot aqueous extraction at 70 ^{0}C. Also, microwave pre-treatment at 400 W for 4 min followed by the cold press was optimized. The moisture content of the peels was determined by 2 h oven drying the peels at 80 ^{0}C

RESULTS AND DISCUSSION

Cold Press assisted Aqueous Extraction of Orange Peel Oil at optimized temperature (CPAQ): The orange peels having initial moisture content of 75 % w/w, when subjected to cold press produced oil, an aqueous phase and solid peel residue, based on the manually applied compression force. The number of cold-press cycles was decided based on the amount of aqueous phase collected and the moisture present in the solid residue of peels. The first cycle of cold press (5 min hold) for 100 g of 2 mm average particle-sized *albedo free* orange peels produced 17.2 g of aqueous emulsion with no visible oil. The second cycle (5 min hold) of cold press produced 3.9 g of aqueous emulsion with no visible oil. The third cycle (5 min) of cold press, however, produced 3.8 g of aqueous phase along with ~0.12 g (Table 1) of orange oil visible on the outside part of cold press plate. After the third cold press cycle no additional amount of aqueous emulsion or oil was expelled. The diagrammatic representation of the CPAE process is given in fig. 1.

Table 1: Cold press assisted oil extraction yield

	Compression % w/w oil	**centrifugation Oil yield**	**Total yield**
CP	0.12	0.05	
CP-AQ	0.67	-----	0.79
MW-CP	0.23	0.07	
MW-CP-AQ	0.52		0.82

Thus, with the three cold-press process, a total of 24.9 g of the aqueous phase was obtained along with a total moisture content of 46.22 ± 3 g in the peel residue. The aqueous phase was an o/w emulsion with oil droplets of 1.2 µm as seen under the microscope. The emulsion had surface tension of 30.8 $mN.m^{-1}$, viscosity 8.5 mPa.s, density 1.0612 $g.cm^{-3}$, and conductivity 3.15 to 5.40 mS cm^{-1} (Table 2**)**. The charge on oil droplet in the aqueous phase studied by electrophoresis was negative, as the oil moved towards the anode. The pH of the aqueous phase was low at 3.5. The HPLC-PDA of the aqueous phase from cold press assisted expulsion showed also the presence of hesperidin, naringin, □- carotene (fig.2 a-b). Settling of the cold pressed aqueous emulsion at 4 ^{0}C for 24 h gave no clear separation of oil. But centrifugation of aqueous emulsion for 1 h at 4 ^{0}C and 20,000 rpm enabled separation of ~0.08 g of oil. The surface tension of the CP aqueous emulsion showed rise from 32.1 $mN.m^{-1}$to 38.9 $mN.m^{-1}$ and the viscosity showed very slight decrease from 8.54 mPa.s to 8.23 mPa.s. There was a very insignificant separation of oil post centrifugation (Table 3). The microscopic observations of the aqueous phase obtained from the cold pressed -centrifuged oil/water emulsion had oil droplets of average size 1.8- 2.5 µm as against 1.2 µm oil droplet size of the emulsion obtained by only CP.

Subjecting the cold-pressed residue to aqueous extraction at optimized temperature (70 ^{0}C) for 1.5 h produced 0.67 g of orange oil at the surface of reaction mass while the untreated orange peels produced no oil even after 24 h of aqueous extraction. Thus cold press followed by aqueous extraction (CPAQ) at 80 ± 2^{0}C gave a total of 0.79 g of orange oil from 100 g of the peels. The compression of peels *with albedo* by cold press produced ~0.05 g of oil and 0.64 g of oil after hot aqueous extraction. The orange peels of 0.16 mm when subjected to CP formed a sticky, moist dough that escaped from the space between the screw press wall and the screw press upper plate and hence produced no oil.

Table 2: Properties of the aqueous phase obtained post cold press and subsequent treatments

Property	**Cold Press**	**CP-Centrifugation**	**MW-CP**	**MW-CP-Centrifugation**	**Water**
Surface Tension (N/m)	0.0308	0.0321	0.0329		0.07286
Viscosity (mPa.s/cP)	8.54	8.50	8.23	8.20	0.89
Density g/cc	1.0612		1.06		0.996
pH .	3.5	3.5	3.5	3.5	4.6
Charge of oil	Negative	Negative	Negative	Negative	---
Oil droplet size (µm)	1.2	1.6, 2.5, 2.8	1.2	1.6, 1.8, 2.5	---
Conductivity (mS)	3.15-5.40		3.15- 5.40		0.05

Table 3: Mass balance of the cold press assisted extraction

Particle size	CP cycle	Yield oil extracted	Solid	Aqueous phase
(mm)	(No. of cycle x min)	% w/w	(g)	(g)
2	1 x 5	-----	82.7	17.2
2	2 x 5	-----	78.9	3.9
2	3 x 5	0.12	75.02	3.8
Total				24.9
2 + MW	3 x 5	0.23	74.00	25.06

Microwave pre-treatment followed by Cold Press aided hot Aqueous extraction at optimized temperature (MW-CP-AQ): The peels subjected to the MW power of 400 W for 4 min followed by CP, produced ~0.23 g of orange oil as against ~0.12 g of oil obtained from CP orange peels without MW pre-treatment. The centrifugation of the aqueous emulsion of MW-CP produced ~0.07 g of oil, indicating no significant improvement in oil separation. The insignificant improvement in the oil yield from the cold pressed aqueous emulsion despite of MW pre-treatment can be because the properties of the cold pressed aqueous emulsion and microwave pre-treated and cold pressed emulsion (surface tension: 32.9 $mN.m^{-1}$ and viscosity: 8.23 mPa.s) were almost similar. An aqueous extraction of the MW –CP peel residue at 80 ± 2^0C, however, produced 0.52 g of orange oil in just 15 min. Thus, the aqueous extraction time was reduced in case of MW -CP compared to CP (1.5 h) alone. The reduced aqueous cooking time is due to the intensive pre-treatment of the peels by the combination of MW and CP methods. However, the oil yield using MW-CP-AQ process is not complete, the MWCPAQ process has enormous steps, which can make the process complex and also incur loss due to handing, making the process less economical. The GC (fig.3) and HPLC (fig.4) result of oil reveals good quality orange peel oil.

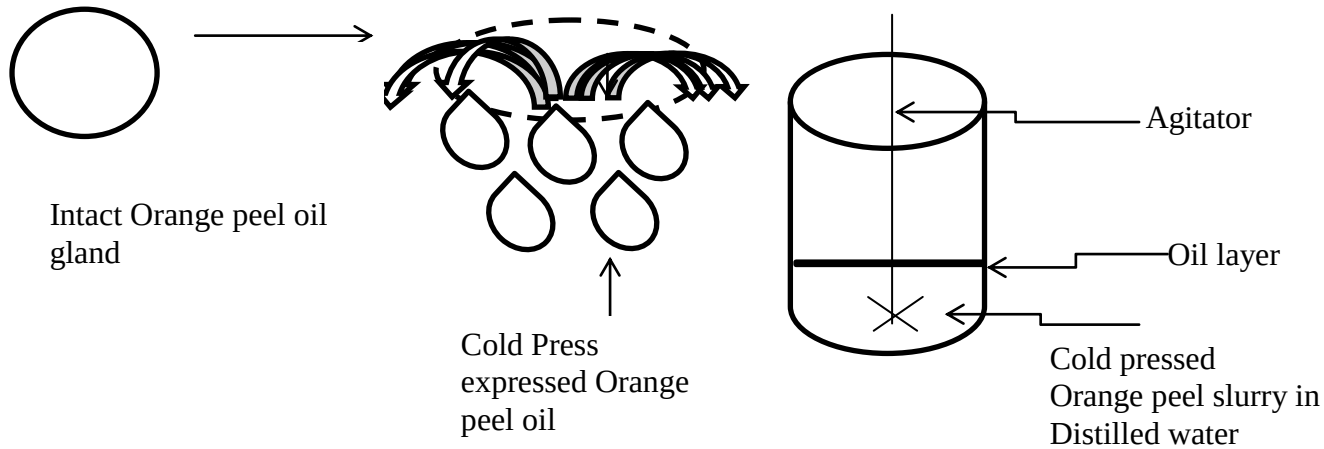

Figure 1: Possible mechanism of orange peel oil extraction by cold press assisted aqueous extraction

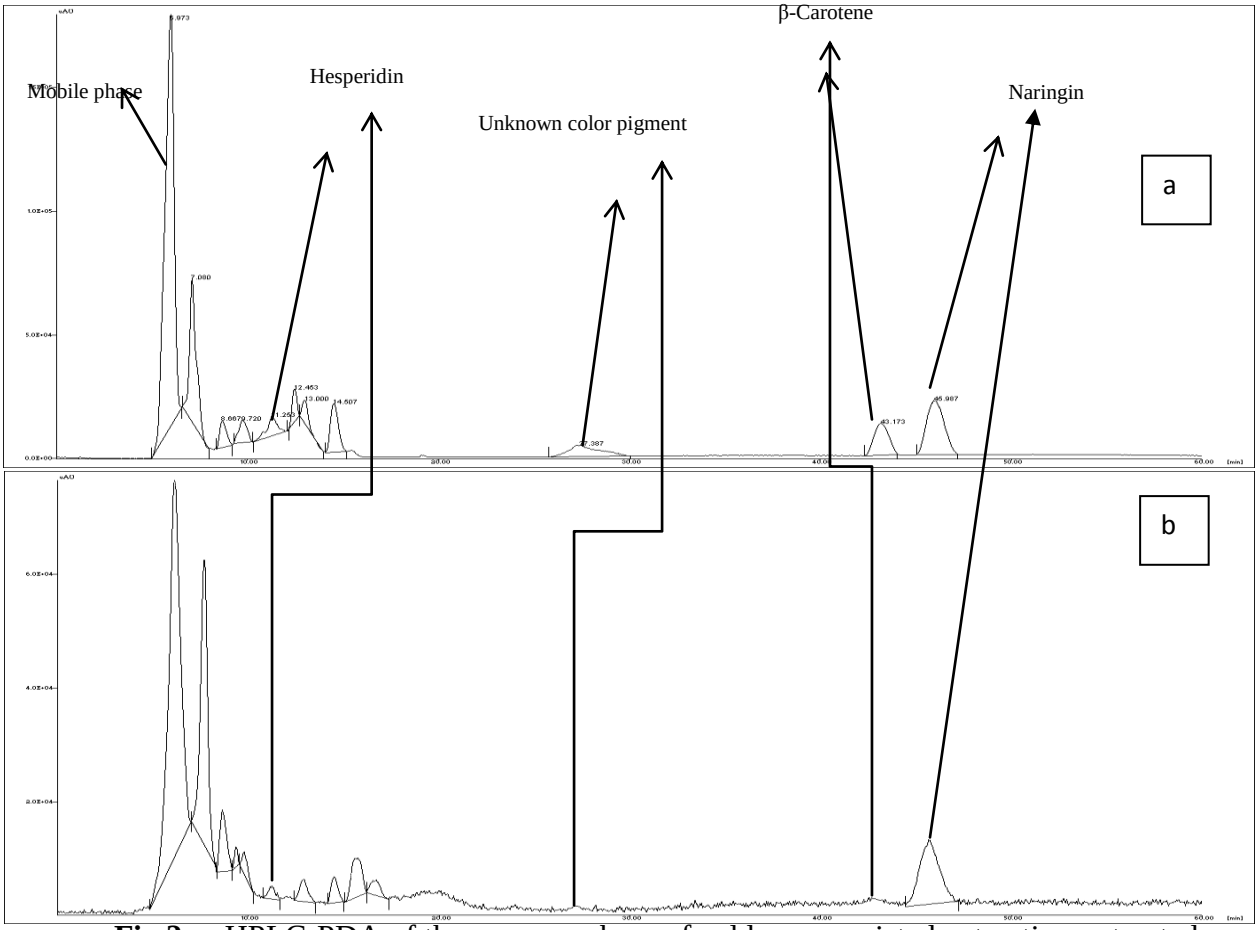

Fig 2 a: HPLC-PDA of the aqueous phase of cold press assisted extraction untreated

b: HPLC-PDA of the aqueous phase of cold press assisted extraction treated with charcoal

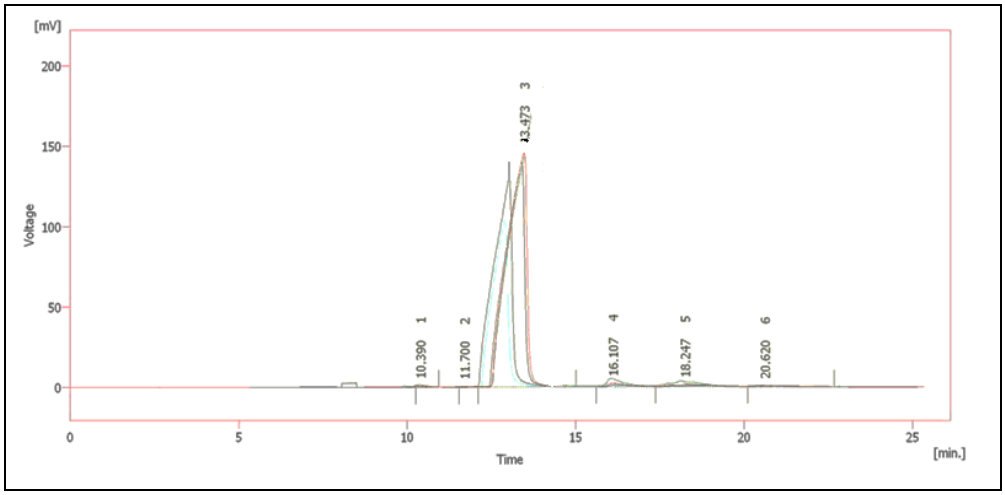

Fig 3: Gas chromatography of MW assisted cold pressed orange oil and Cold pressed orange oil (1. α-Pinene, 2. Myrcene, 3. Limonene (~96.3 %), 4. Limonene oxide, 5. Linalool, 6. Citronellal)

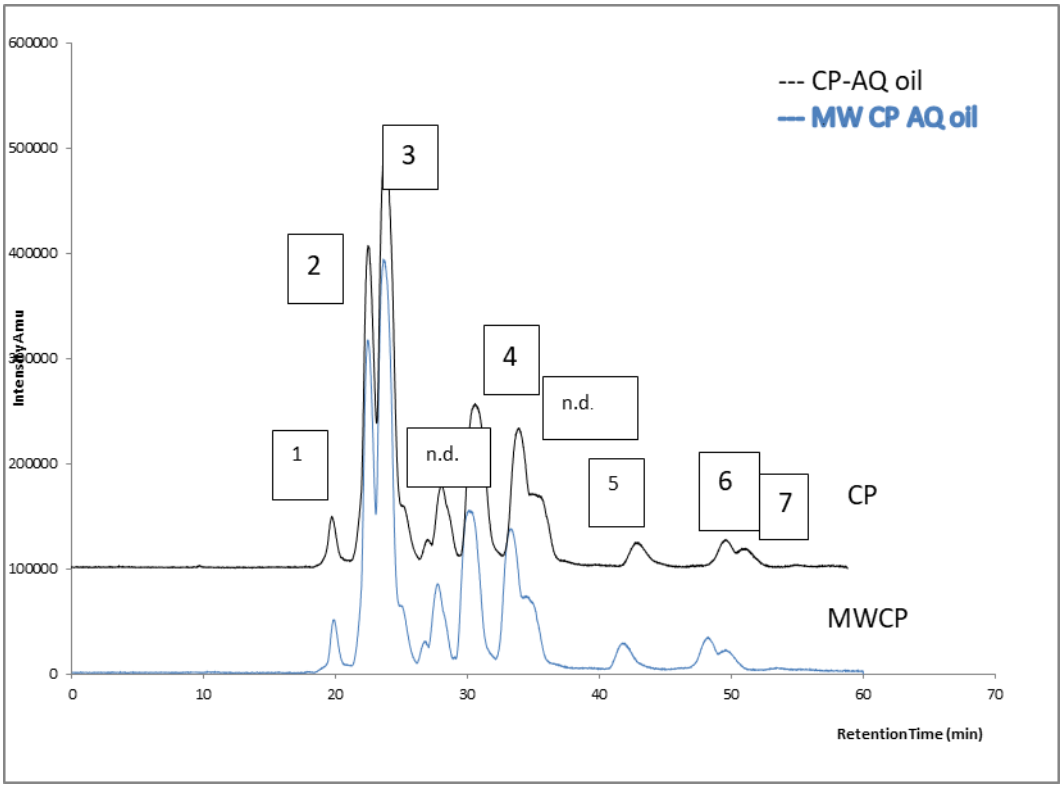

Fig 4: High performance liquid chromatography of MW assisted cold pressed orange oil and Cold press orange peel oil (1. Tangeritin, 2. Sinensetin, 3. Nobiletin, 4. Tocotrienol, 5. Tocopherol acetate, 6. Xanthophyll, 7. 3- hydroxyl α-carotene)

DISCUSSION

Ikechukwu et al.[9], Venter et al.[10], and Deli et al.[11], have reported that the efficiency of the cold press or the number of cycles required to expel maximum material is dependent on the design of press, the pore size of the perforated plate placed at the bottom of the cold press and the pressure applied to discharge the aqueous phase from solid orange peels [8-10]. The low pH-value of the cold pressed expressed emulsion phase could be related to solubilization of ascorbic acid and citric acid from the peel to aqueous phase during compression of peel. Torrado et al.[12] have reported production of citric acid by fermentation of the orange peels and have reported that citric acid is the reason for the lower pH of the aqueous phases. Hence, pH 3.5 obtained in the current research findings was assumed to be related to the presence of citric acid.

The results obtained for surface tension, viscosity, pH and the charge of oil phase in the emulsion indicated that the aqueous emulsion was very stable [13]. The stability of the emulsion can also be related to "dissolved components" including pectin, hesperidin, naringin, carotene which could be behaving as emulsifiers. Coll et al.[3], have used enzymes and centrifuge to destabilize the emulsion obtained from cold-pressed orange peels to recover citrus oil. The reason for insignificant oil separation post high speed centrifugation might be because of settling of the heavier components and insignificant changes in the viscosity, surface tension and oil droplet size of the CP-aqueous emulsion. Gernonet al., [13] has also indicated in their research work that centrifugation assists de-emulsification. The microscopic of the emulsion oil droplet size also indicates poor destabilization of emulsion post centrifugation.

The yield of CP treated orange oil was less compared to the oil yield obtained by the standard n-hexane assisted extraction method (1.0 g), which can be attributed to the losses due to the need of vigorous handling for CP (three-cycles of compression).
The reduced oil extraction from peels having *albedo* was possibly because *albedo* contributes to approximately 8-10 % of the total peels mass and also absorbs the oil due to its high cellulose content[13-14].

The peels with particle size below 0.2 mm formed an incompressible sticky mass with no oil yield. The peels of 1 x 1 cm square size when compressed produced only 4 g of the aqueous phase and no oil. The reduced average particle size improves the efficiency of the extraction [15-16]. Bachman [18], Ogunsina [19], have stated, as per the design of the press, the optimum particle size of the raw material varies.

CONCLUSION

The developed process elucidates possible reasons for the poor yield of orange oil by CP method. The reason for the poor yield has been related to formation of a stable emulsion of the aqueous phase collected post CP. The physical properties of aqueous phase obtained after CP such as the surface tension, viscosity, density, charge, size of oil droplet, conductivity give indications for a stable emulsion. Also, the chemical composition as studied by HPLC shows the presence of molecules such as naringin, hesperidin which can be the reason for stable emulsion to be obtained by CP and poor oil yield after CP. The optimum parameters for the CP-AQ obtained were three CP cycles, aqueous heating at 70 ^{0}C for 1.5 h. The developed CP-AE process uses simple stainless steel screw press for CP and a baffled glass reactor with an agitator to perform AE at milder temperatures, lower agitation speed, and at reduced extraction time compared available methods. Thus, the developed process has eliminated the use of enzyme or solvent or centrifuge or higher temperature required for conventional processes. This makes the developed process green and an alternative to available orange peel oil extraction methods.

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