Techno economic Evaluation of Clean Technologies for Waste Minimization in Herbal Extraction Industry

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Abstract- There is wide range of operation and processes as diverse as its products in pharmaceutical industries and effluents generated from these processes vary from one industry to other. As these processes consumes variety of toxic chemicals, the effluents generated are complex in nature and are not easily treatable by the conventional methods of treatment. The current study has been undertaken to evaluate techno economically clean technologies with in process which are resulting into pollution load reduction at the end pipe of treatment and reduction in emissions. Presently in most of the extraction processes conventional methods such as solvent extraction, steam distillation and hot water extraction etc are involved. However due to stricter environmental regulations use of green technology replacing conventional extractions methods is gaining momentum. The industry selected for study is manufacturing Colochicine and Thiocolochocide by processing Gloriosa Superba seeds, a herb traditionally used for treatment of various clinical conditions like inflammation, edema, skin infections and many others. Accordingly the aim of the paper is to present work ability of replacing conventional solvent extraction with super fluid CO_2 extraction up to syrup stage with in process and environment friendly techniques. Being a green solvent the effect on herbal extraction suggests the use of pressure and temperature in the range of 350mm-450mm and temperature up to 65^{o}C respectively. The major components of extracted material were identified as syrup and has been has further subjected to purification and crystallization besides resulting into 60% reduction in case of waste water generation per kg of product and same level of reduction in SO_2 emissions from sources using the pet coke or coal as fuel.

Key Words-COD(Chemical oxygen demand),BOD-(Bio-Chemical oxygen demand),SFE (Supercritical fluid extraction), MBR(Membrane bio-reactor),HPLC(High Performance liquid chromatography), WWG(Waste water generation),MDC(Methlyne Di Chloride)

1.0 INTRODUCTION

As already stated that due to enforcement of stricter environmental legislation, the super fluid extraction is becoming popular in recent years as an alternative to the conventional extraction Qingyong et al.(2000). The treatment of waste waters from pharmaceutical industries including herbal extraction to the prescribed standards has always a challenge due to use of wide variety of toxic chemicals in the process Chia-Yuan Chang et al.(2008).

Moreover the awareness of bad effect on use of synthetic chemicals has enhanced the demand and consumption of herbal products. In order to cope with increasing demands of herbal products, a highly innovative herbal processing techniques have been inducted to produce the optimal amount of activated ingredients Siti Nuurul et al.(2016). The traditional method of boiling herbs requires longer extraction time to obtain photochemical. So the advance methods of extraction such as microwave assisted extraction Kaufman.B etal.(2002), sonication assisted extraction Vinatoru et al.(2001)and ultra-high pressure extraction Xi.J et al.(2009) Shoquin.Zet al.(2004), hot water extraction Ayala.R.S et al.(2001) and Ozel.M.Zet al. (2003) have been used to perform faster extraction and obtain higher yield. There is considerable decrease in extraction time as these techniques operate at higher pressure and/or pressures. Moreover these advance techniques require higher capital investment due to complexity of equipment and observed in very limited application. The work for research is in progress to better understand the different types of extraction mechanism with the objective to improve the efficiencies and cost effectiveness. Apart from these advance techniques supercritical fluid extraction is one of the efficient and effective method in herbal processing due to its ability to extract the valuable ingredients with more yield and better quality Bernardo-Gilet al.(2011). In case of Super Fluid Extraction less environmentally unfriendly organic solvents are not used. Negligible quantity of organic solvents are being consumed whereas usually in liquid-solid extraction method would require tens to hundreds of milliliters I.R Wheeler et al.(1989) A.Otterbach et al.(1999). Accordingly in this category of industry supercritical fluid extraction(SFE) has been considered as better clean tech option, Which has been widely accepted in recent years and shall be effective as a substitute to conventional extraction for separation of organic compounds in Herbal extraction and API drugs manufacturing units. In case of large SFE processes, very less waste generation due to the fact that CO_2 in fluid form can be recycled or reused. The substance is termed as supercritical when its pressure and temperature are greater than its critical pressure and temperature. For herbal extraction and pharmaceutical applications CO_2 is an ideal processing medium. Furthermore carbon dioxide is nontoxic, non-flammable, comparatively inexpensive, recyclable and generally considered as safe solvent. Among all the fluids studied, CO_2 remains extensively used fluid for the applications as SFE, because at low critical temperature and pressure, it attains non toxic and non-flame able properties.

The super fluid extraction systems of different scales can be implemented in different levels. In addition to this the CO_2 as supercritical fluid has good solvent characteristics for extraction of non polar compounds such as hydrocarbons, while its large quadruple moment also permits it to dissolve some temperately polar compounds such as alcohols, esters, formaldehyde and ketones. Use of CO_2 for extraction causing into minimal pollution load can finally lead to recycling of treated effluent into process and utilities, in case of implementation of advance end of pipe treatment options such as MBR coupled with ozonation.

This method has several benefits such as easy extraction, minimum loss of materials, end product of high quality besides retaining explosive constituents E.Ibanez et al.(1999). This technique has gained importance in producing essence because of change in process and also the obtain ability of cheap raw material and low labor cost besides demand for high quality products globally. In the literature review serious concern of economic aspect of SFE has been taken into consideration, but they are either focused on particular regions of Latin America P.T.V Rosa et al. (2005) and dealing with extraction based on use of liquefied gases J.C Crause et al.(2003) has conducted surveys with the outcome that the cost of manufacturing of extracts produced by SFE were less in comparison those produced through conventional distillation. SFE can not be simply supported by laboratory data. While designing and recommending industrial unit of extraction, mass transfer parameters are carefully taken into account, Whereas the complete industrial processes may encounter with problems such as fluid channelizing, pressure drop agglomeration of the material, the laboratory data could be sufficient with less error for economic analysis.

2.0EXPERIMENT (Super Critical Fluid CO_2 Extraction)

The unit engaged in herbal oil extraction was selected in order to study techno-economic feasibility besides comparative evaluation of environmental impacts of CO_2 and conventional extraction techniques. The unit with pilot scale CO_2 equipment was selected for study is extracting syrup from aromatics medicinal products. The photograph of the pilot plant for extraction of oil has been shown as below in Fig-1

Fig-1 CO_2 Extraction Unit

The unit is manufacturing the anticancer products such as Thiocolchicoside and Colchicine each with production capacities of 1200 kg/year using gloriosa superb seeds as raw material with monthly consumption of 20 metric tons.The unit has been selected to carry out study for replacement of conventional extraction method with super critical fluid (CO_2) extraction, which has been used for manufacturing of herbal products in recent years and can be considered as best option for extraction of colochicine having higher content in gloriosa seeds. Colchicine which was further approved by the food and drug administration (FDA,USA) as a drug for gouts in the year 2009 and in liquid form as a single ingredient in the year 2019. The main objective of the study was to evaluate techno economic feasibility of using this green technology as an alternative to conventional solvent extraction techniques.

The following extractor operating conditions were measured during the study

- CO_2 flow rate
- CO_2 pressure
- Extractor temperature
- Weight of the sample

The experiments were carried out at pilot scale unit installed for testing 1kg of raw material sample. The schematic conceptualized diagram of super critical fluid extractor has been shown in

Fig-2 as below. Without any pre treatment the sample of app 1 kg of gloriosa superba seeds were extracted using super critical CO_2 apparatus by increasing temperature up to 65^{o}C and

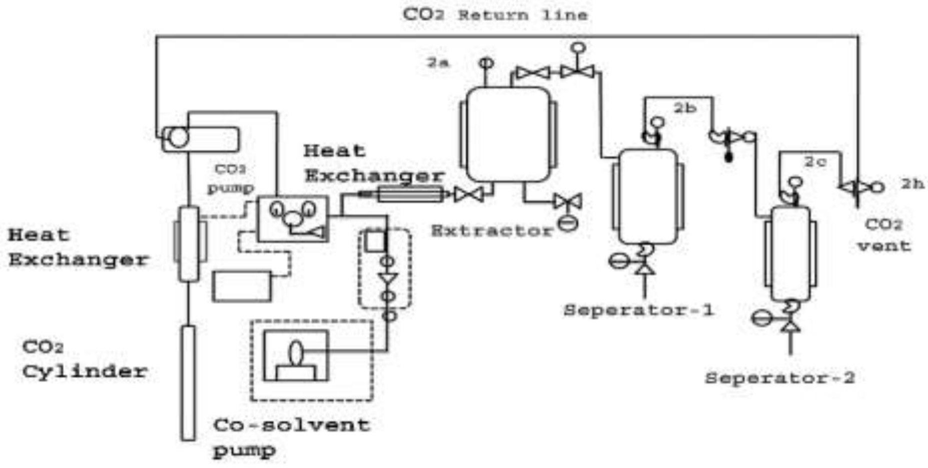


Fig-2 Schematic flow diagram of CO_2 Extraction Unit

varying pressures in the range of (200-450) bars. Seeds of Gloriosa Superba were grounded in pulveriser and placed in the air tight extractor in order to avoid entry of air . Different pressures and temperatures were maintained in the separators in the range of (200-450) bars and at constant temperature. Seeds of Gloriosa Superba were grounded in pulveriser and placed in the air tight extractor in order to avoid entry of air. Having different pressures at constant temperature were maintained in the separators in the range of(200-450) bar at 65^{o}C respectively. Thereafter , the extract was collected in separator-1, while wax material, fatty acids and other volatile materials were collected in separator-2. The extraction was carried out with liquid CO_2 and 3% water used as co-solvent. The extraction rate is enhanced due to use of water as co solvent which can be removed further by applying low pressure during the period it is transferred to the separator 2. The heating/cooling systems were turned on after placing the basket containing seeds powder inside the extractor. The liquid CO_2 flow rate was kept at a constant 100gramme/minute and 3g of water is added as co-solvent used as extraction media. Once the temperature of extraction cylinder reached up to 65^{o}C, all the pressure valves as shown in the Fig-2 are opened. The each extraction is carried out for 3 hour in order to observe the yield at different pressures was analyzed as per data shown in Table-1

Table-1- Gloriosa superba extraction and yield correlation

Sl No	Exp No	Gloriosa Seeds Loaded(Kg)	Pressure of Extractor	Temperature(^{o}C)	Flow rate of liquid CO_2(g/min)(3% Water as Co-Solvent)	Yield(G)	Assay of Colochine (HPLC) (%)
1	1	1	200	65	100	0.45	Nil Waxy
2	2	1	250	65	100	1.7	3.0
3	3	1	300	65	100	3.43	6.92
4	4	1	350	65	100	18.73	20.3
5	5	1	400	65	100	24.8	27.0
6	6	1	450	65	100	26.76	16.15

3.0 Results and Discussions

The graphs shown in Fig-3 between pressure in the extractor and yield of Gloriosa syrup indicates that maximum extraction (26.76g) is achieved at a pressure of 450mm and at a temperature of 65 ^{o}C which are higher than optimum levels required for maximum yield at a pressure and temperature at 350mm and 65^{o}C respectively without using any co solvent, however in this experiment water has been used as co solvent for extraction of syrup at a temperature and pressure of 65^{o}C and 450mm respectively. The value of R^2=0.907 is best fitted in the curve indicating better correlation between operating pressures and yield at different levels. The variation of values in case of yield is almost having similar trend as for pressure with minute variation in the graph.The value of R^2 = 0.562 shown in Fig-4 that max assay of colochicine (%) is recovered from the mass is at a temperature of 65^{o}C and at a pressure of 400 mm, however beyond these values there is sudden decrease in colochicine mass% recovered against linear trend in values of pressure as shown in the Fig-5 is again showing similar trend with value of R^2=0.9174 for yield R^2 = 0.5629 for %mass of colochicine recovered. For 1 kg of product by conventional solvent extraction and supercritical fluid extraction the quantities of solvents and CO_2 as supercritical fluid extraction has been observed as 7-10 and 0.7-1litre respectively .

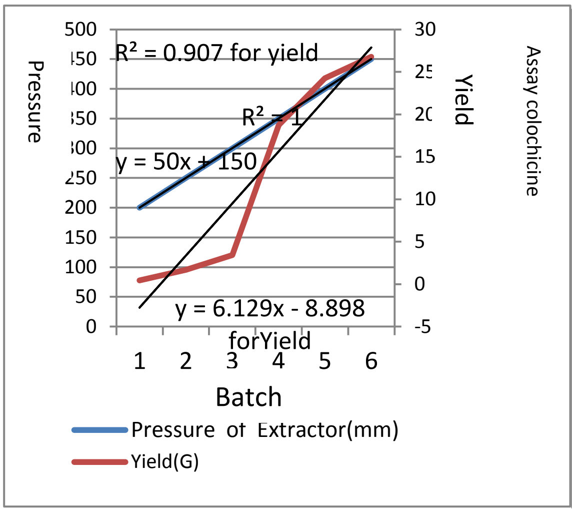


Fig-3:Graph between Pressure and Yield

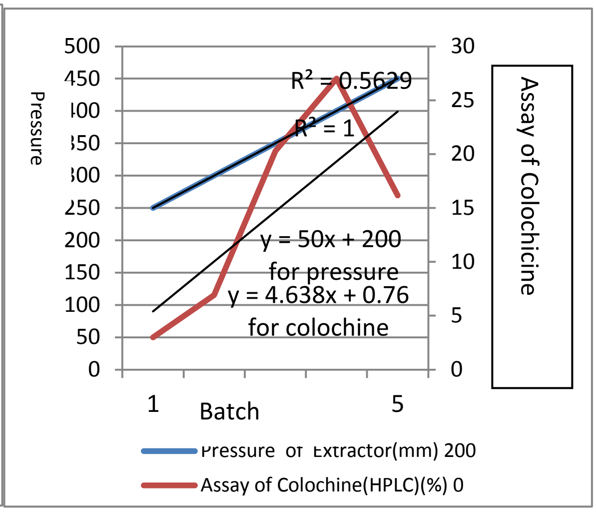


Fig-4: Graph between Pressure and Assay of Colochocine

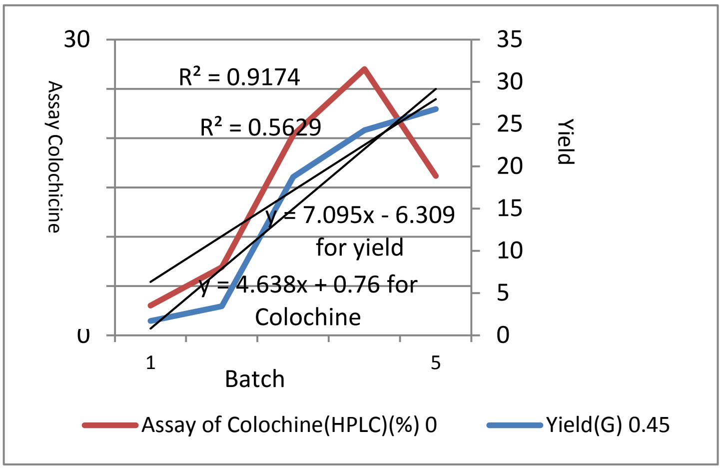


Fig-5: Graph between assay of Colochicine and yield

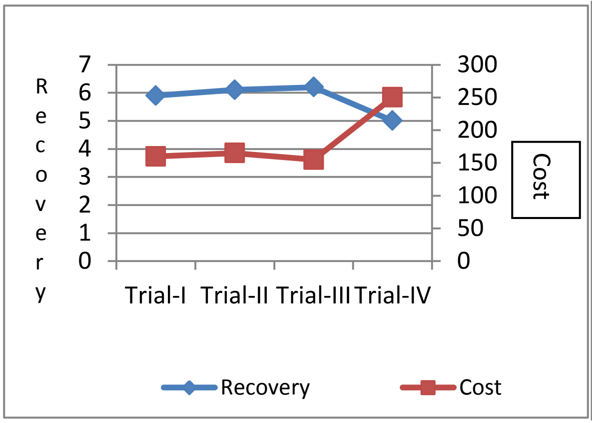
3.1 ASSAY OF COLCHICINE

The supercritical CO_2 has a good solvent properties for its non polar nature with adequate extraction as the product colchicine has higher molecular weight. The material recovered from extraction in syrup form has been further subjected to purification and finally crystallization using ethanol,ethyl acetate,methylene di-chloride and chloroform as solvents in three trials (Trial-I, Trial-II and Trial-III) through HPLC. Finally the percentage purity and quantity of material recovered after separation, purification and crystallization from all these trials using (Ethanol+Ethyl Acetate),(MDC+Ethyl Acetate) and (Chloroform+ MDC+Ethyl Acetate) has been shown in the Table-2. The quantities of material recovered, cost of production per kg of raw material processed and waste water generation(WWG) per kg of product have also been shown in Table-2 the outcome of results from these three trials were further compared with the conventional extraction as Trial-IV followed by purification and crystallization at industrial scale for carrying out techno-economical evaluation.In Trial IV for extraction of syrup ethyl acetate and ethanol are being used further separated,purified and crystallized with the same solvents for trials mentioned as above .

3.2 Techno economic Comparative Evaluation

The relationship between material recovered, cost of production, waste water generation, recovery and purity levels for all trials have been shown in Figures- 6,7,8 and 9 where it is clearly indicated that recovery level with CO_2 extraction is on the higher side in comparison to conventional extraction. Moreover the waste water generation is comparatively reduced to almost 60% in case using CO_2 as SFE medium with co solvents which are having higher anti risk rankings such as ethanol and ethyl acetate having lesser impact on the environment ,whereas in case of chloroform as co solvent the reduction in waste water generation is although about 85% but higher pollution load due to low anti risk rankings . Moreover lower costs of production have been observed in case of super fluid extraction in comparison to conventional extraction in all the trials. Since in the Trial-II and III the MDC (methylene di chloride) and chloroform along with ethyl acetate have been used in process of separation, purification and crystallization , the residues with higher toxicity levels shall be generated whereas the solvents such as ethyl acetate and ethanol used in case of Trial-I are environmentally friendly having anti risk ranking higher than MDC (methylene di chloride) and chloroform besides having lower hazard potential.

Sl No	Table-2- Techno- economic evaluation of trials for extraction of colchicine					
	Trial	**Extraction/ Purification**	Recovery in (G)	Cost/kg of processed Raw Material(Rs)	WWG(KL)/kg of product	Purity Levels in (%)
1	I	CO_2/ Ethanol+Ethyl Acetate	5.9	160	1.4	99.82%
2	II	CO_2 /MDC+Ethyl Acetate	6.1	165	1.5	99.24%
3	III	CO_2/ Chloroform+ MDC+Ethyl Acetate	6.2	155	0.5	99.10%
4	IV	Convention Extraction	5	259	4	98%



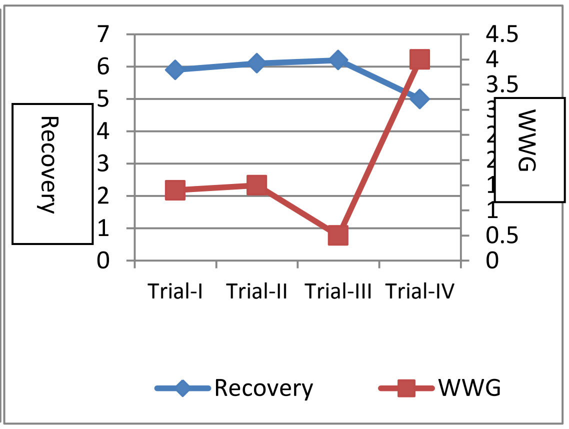


Fig-6 Graph showing relationship between recovery and cost

Fig-7 Graph showing relationship between recovery and WWG

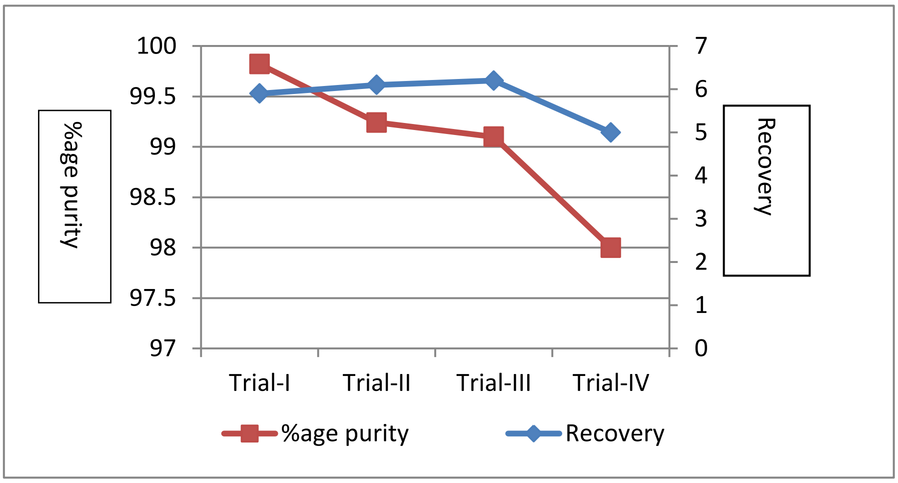


Fig-8 Graphs showing relationship between material recovered and %age purity

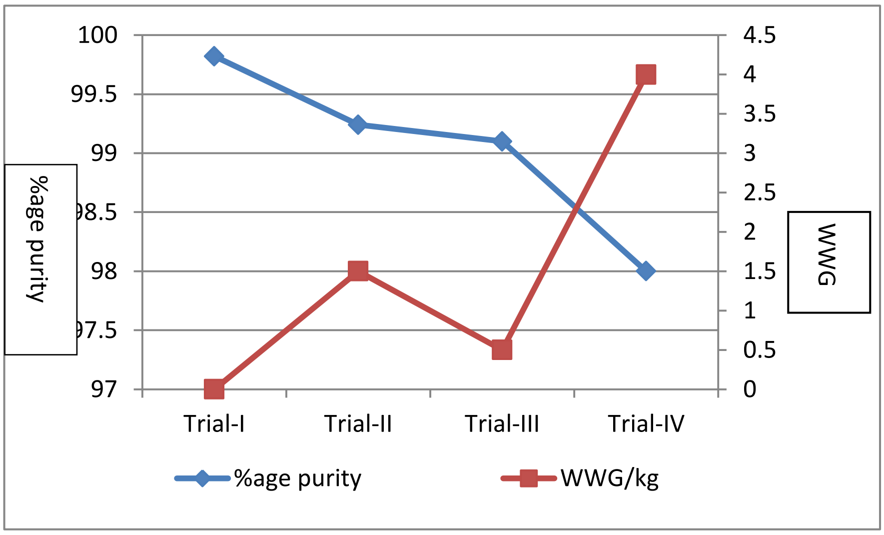


Fig-9 Graphs showing relationship between %age purity and WWG/kg

Based on field surveys and data collected the comparative production cost between conventional extraction by solvents , Super Fluid Extraction(CO_2) and separation cum purification has been carried out and shown in the Table-3 where labour cost, energy, fuel, chemicals and misc expenses have been taken into consideration-

Table -3:Techno Economic Evaluation(Processing cost/kg of raw material)

Sl No	Components	Conventional Extraction, Separation and Purification (Rs)	CO_2 Extraction (Rs)	Separation and Purification (Rs)	Conventional Extraction (Rs)
1	Labour	96	24	60	36
2	Energy	60	12	36	24
3	Fuel	22	6	14	8
4	Chemicals	55	13	34	21
5	Misc	26	6	16	10
	Total	259	61	160	99

The data summarized in the Table-3 clearly indicates that manufacturing costs in case of CO_2 extraction from Gloriosa Superba Seeds is Rs 61 per kg of raw material processed in comparison to Rs 99 per kg for conventional extraction systems. Moreover this has been proved in case of rosemary plant Mojtaba et.al.(2009) that manufacturing costs of the extracts produced by the SFE were lower than those produced by the conventional methods. Normally the operating costs are comprised of raw material, labour, chemicals,CO_2 and utilities such as boilers, compressor and chilling tower etc. However by considering same properties of the raw material in both the extraction systems, the manufacturing costs taken into consideration are comprised of components mentioned in the Table-3 such as labour, energy, fuel, chemicals, CO_2 and misc expenses. The only disadvantage in installation of SFE plant is higher equipment cost. For the plants having manufacturing capacities 500-600kg/month , the investment of rupees 4.5-6.0 crore shall be involved which is very high compare to conventional extraction system. The major advantage of these plants is lower manufacturing costs resulting into benefit of Rs 38/kg of raw material processed over conventional extraction system.

In case of the unit selected for this study is consuming 20 MT/month of Gloriosa Seeds, the net annual gain of Rs 1crore and 15 lacs can be achieved. And comparing these gains over equipment cost the pay back period of 3-4 years is ensured which is a workable option besides lesser impacts on environment and can yield carbon foot prints besides having further scope for curtailing said pay period at plant scale where higher yield of extracted material in case of injecting intensification measures are coupled with super fluid extraction systems. The payback period can be further reduced by increasing yield through enhancement in extraction efficiencies

So the solvents such as ethanol and ethyl acetate are environmentally safe irrespective of the fact that recovery of final product is higher in Trial-II and Trial-III besides lower waste water generations. But keeping into consideration the safety and compliance to environmental requirements the combination of solvents involved in Trial-I are acceptable.

Another added advantage of CO_2 extraction is saving in energy cost as no steam required in the case SFE method and fuel consumption is almost negligible. Apart from increased yield from the CO_2 extraction there shall be overall reduction in steam consumption resulting into energy saving. Since the material extracted by using CO_2 have high purity due to less residues, the steam consumption shall be further reduced in separation and purification processes. Accordingly over all 60% saving of fuel in the boiler for steam generation can be ensured. The over all consumption of pet coke shall be reduced to 750kg/day against consumption of 2.5 T/day in case of conventional extraction system which shall ultimately resulting into reduction of SO_2 emission calculated as below.

Assuming 5% of sulphur content in the pet coke, the emission rate of SO_2 in case of conventional extraction system $0.05\times\frac{2500}{24}$= 5.20 kg/hour accordingly $S+O_2$=10.40kg/hr, where as same shall be reduced to 4.16 kg/hr after the implementation of CO_2 as Super Fluid Extraction Solvent.

4.0 CONCLUSION AND RECOMMENDATIONS

The study conducted reflects the herbal processing of Gloriosa Superba seeds by Super Fluid extraction using CO_2 as green solvent. Rapid implementation SFE techniques is being expected in future for extraction and separation of active compounds from herbal plants. Moreover considering the availability of herbal plants, inexpensive labor, lower energy consumption , nominal use of toxic chemicals have been observed as feasible option. Based on the facts stated as above SFE can be implemented on wide scale. Apart from reduction in pollution load in terms of effluents and emissions the SFE process is economical and from the outcome of research ,it has been observed that manufacturing cost in case of herbal extraction by CO_2 is Rs 61/kg of raw material processed in comparison to Rs 99 per kg for conventional extraction system.It has also been observed that replacing conventional extraction with CO_2 as super fluid has resulted into 60% reduction in case of waste water generation per kg of product and same level of reduction in SO_2 emissions.

5.0 References

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