EXTRACTION OF ATILI (BLACKDATE) OIL FROM THE PULP USING AQUEOUS BIPHASE SYSTEM

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ABSTRACT
In this research, Atili (blackdate) oil (Canarium Schweinfurthii) was extracted from the pulp using aqueous biphasic system (ABS) prepared from fixed concentration (40%) of polyethylene glycol (PEG) and varying concentrations of salt (di-sodium hydrogen phosphate (Na_2HPO_4)) at 10%, 20%, 30%, 40% and 50% respectively. The partitioning of the atili oil to the PEG-rich phase for the various combinations of the salt concentration with the fixed PEG concentration were compared and the extracted atili oil characterized. The extraction process was carried out by preparing the aqueous biphasic systems with the varying salt concentrations and placing the enclosed pulp of atili fruit inside the ABS prepared until the oil partitions to the PEG-rich phase. The ABS prepared from the salt concentration at 20% was found to give the best system for extracting atili oil with a yield of 43.50 mls of atili oil /100g of atili pulp. Lastly, the acid value , saponification value, free fatty acid and ester values were found to be 0.22, 116.13, 0.11 and 115.92 respectively.

Keywords: *Atili, extraction, oil, aqueous, biphase*

1.0 INTRODUCTION

Aqueous biphasic systems are clean alternatives for traditional, organic-water solvent extraction systems formed when two polymers, one polymer and one kosmotropic salt, or two salts (one chaotropic and the other kosmotropic salt) are mixed together at appropriate concentrations or at a particular temperature. The two phases are mostly composed of water and non-volatile components thus eliminating volatile organic compounds (McCabe, *et al*, 2005). Liquid-liquid extraction is a process of separating components in solution by their distribution between two immiscible liquid phases. Such a process can also be simply reffered to as *liquid extraction* or *solvent extraction* (Perry and Green, 2008). Atili (*Canarium schweinfurthii bursaraceae*) is the fruit of the perennial tree plant also called Atili tree. In Nigeria, the fruit is called 'ube okpoko' in Ibo and "atili" in Hausa. The fruit is commonly found in large quantity in Pankshin, Plateau State of Nigeria and is also produced in similar quantities in other states of the northern and south-eastern Nigeria (Agu, *et al*, 2008). Atili oil is the oil extracted from the mesocarp of the atili fruit. It is rich in fat, protein, carbohydrate, and water and sometimes, ash in low quantity (Damilola, 2011). In the savannah part of Nigeria, they are often cultivated for their fruit which are edible, purplish, ellipsoid but slightly three-angled. Generally, the fruits are boiled and eaten without much value for the oil content. However, among the "Kama" tribe of Adamawa state and "Mwaghavul" of Plateau state in Nigeria, they have extracted the oil from the seeds and fruits of Atili and used in crude form for cooking and body cream. A lot of interests have been generated by recent studies on the chemical composition of the fruits (Eromosele, *et al*, 1991) and the seeds (Eromosele and Eromosele, 1993) of some wild plants. Figure 1 shows the Atili fruit and seeds.

In Biotechnology, many of the usual organic solvents will degrade a sensitive product such as protein; this has led to the use of "mild" aqueous-based extractants, such as water-polyethylene glycol-phosphates mixtures which will partition and concentrate the product in one of the two aqueous layers which are formed (Richardson, *et al*, 2002). The aim of this work is to extract oil from Atili (Blackdate) fruit using an aqueous biphase system and to characterize the oil extracted.

(a) (b)

Figure 1 The Atili (Blackdate) (a) fruit (b) seed

2.0 MATERIALS AND METHODS

The fruits were sorted to remove any dirt or foreign materials present in them. They were then, washed in cold water. The fruits were packed in a clean bowl and hot water at 65°C was poured into the bowl and left for five minutes to soften the tissue of the fruits. The fruit was pound in a mortar and pestle for ten minutes and the seeds manually separated from the pulp. Figure 2 shows the pound Atili fruits.

The aqueous biphase system was prepared by mixing each of the prepared solutions of varied concentration of di-sodium hydrogen phosphate (Na_2HPO_4) and polyethylene glycol (PEG3350) solution (40w/w%), at a ratio PEG/salt of 1:1. The solution was then shaken for 30seconds to facilitate proper mixing and then allowed to settle into two seperate phases. To each of the freshly prepared ABS, of varied salt concentrations, 50g of the Atili pulp was wrapped with a filter paper and inserted into the 250mls beakers and allowed to stand until, the oil selectively partitions into the polymer phase; this became the loaded phase. The resulting loaded phase was then decanted from the salt-rich phase and the polymer recovered (see Figure 3) from the loaded phase leaving behind a high concentration of the oil

Figure 2 Atili fruits (a) pound pulp

(b) maually seperated pulp

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Figure 3 Set-up (a) Before partioning

(b) After partitioning for the five varied concentrations of salt

The loaded polymer phase decanted was contacted with/or mixed with a water immiscible organic solvent (butanol) resulting in the generation of an oil/ water system comprised of an organic phase (less dense), and an aqueous polymer rich-phase (more dense). The non-ionic oil partitions to the organic phase, resulting in a high concentration of the oil in the organic phase. The extracted oil, which was soluble in the organic solvent, remains in the aqueous solution. A substantially salt-free organic solution containing a high concentration of oil and an aqueous solution containing a high concentration of the polymer were recovered. The chemical and physical properties of the Atili oil were determined with a view to characterize the oil. The major properties determined using the method described by IUPAC, (1979) include the density, refractive index, viscosity, saponification value, ester value, and iodine value (Kamalu, 2005). The proximate analysis of the fruit was also carried out.

3.0 RESULTS AND DISCUSSION

Table 1 shows the amounts of upper and lower phases formed after the PEG-rich phase was decanted from the salt-rich phase.

TABLE 1: VOLUMES/AMOUNTS OF UPPER AND LOWER PHASES FORMED

Sample	Upper phase (mls)	Lower phase (mls)	Miscella (g)
I	132.00	39.00	71.61
II	72.00	85.00	83.42
III	89.00	53.00	81.85
IV	82.00	49.00	83.34
V	54.00	88.00	77.49

*NOTE: The sample numbers in the table refer to the following mixture of PEG and salt solutions in w/w% as follows: I- 40% PEG- 10%Na_2HPO_4, II-40% PEG-20%Na_2HPO_4, III-40% PEG- 30%Na_2HPO_4, IV-40% PEG- 40%Na_2HPO_4 and V-40% PEG- 50%Na_2HPO_4

It can be seen that, an increase in concentration of salt from 10%w/w to 20%w/w led to a sharp decrease in the quantity of the PEG-rich phase from 132mls to 72mls but the PEG-rich phase with the salt concentration was observed to be more loaded based on the colour of the PEG-rich phase. The increase in the loading/partitioning of the PEG-rich phase suggests an increase in partition coefficient (Singh, 2010). In addition, as the salt concentration was increased further from 20%w/w to 30%w/w, there was a slight increase in the quantity of the PEG-rich phase from 72mls to 89mls since change in phosphate concentration influences the ionic strength of phase and hence partition coefficient of oil (Singh, 2010). However, when the concentration was increased beyond 30%w/w to 50%w/w, the quantity of the PEG-rich phase decreased from 89mls to 54mls. This drop suggests that the high salt concentration is responsible for the reduced distribution of the target extractant into the PEG-rich phase. It therefore means, increasing the concentration of the salt can increase partitioning to an optimum beyond which any increase will affect or decrease the partition strength. Table 2 shows the yield of oil from 100g of pulp used for the different salt concentration. It was deduced that the best salt concentration for the extraction of Atili oil was 20%w/w of salt with recovery of 43.5mls of oil. This is therefore the optimum beyond which increase in salt concentration would result in the decrease in the yield and the partition strength. Tables 3 and 4 show the results obtained for the moisture and ash content tests respectively. From these data, the moisture and ash contents were calculated as 2.20% and 6.10% respectively. These values are consistent with those from literature (Agu, *et al*, 2008). Table 5 shows the chemical properties of the atili oil extracted. The acid value was calculated as 0.22.

TABLE 2: RECOVERY OF POLYMER FROM LOADED PHASE

SAMPLE	BUTANOL USED (mls)	POLYMER + SALT RECOVERED (mls)	BUTANOL + OIL (mls)	OIL (mls)
I	50.00	124.00	58.00	8.00
II	40.00	28.50	83.50	43.50
III	40.00	51.5	77.50	37.50
IV	40.00	48.50	73.50	33.50
V	40.00	10.50	83.50	43.50

TABLE 3: MOISTURE CONTENT TEST RESULTS

RUNS	WEIGHT OF POUND PULP(g)	WEIGHT OF PULP AFTER DRYING W_1 (g)	MOISTURE CONTENT (%)
I	10.00	9.782	0.218
II	10.00	9.778	0.222
Average	10.00	9.78	0.220

TABLE 4: ASH CONTENT TEST RESULTS

RUN	WEIGHT OF DEHYDRATED PULP,W (g)	WEIGHT OF PULP AFTER DRYING, W_1 (g)	WEIGHT OF ASH ($W-W_1$) (g)	ASH CONTENT (%)
I	9.7820	9.1610	0.6210	6.3484
II	9.7780	9.2040	0.5740	5.8703
Average	9.7800	9.1825	0.5975	6.1094

TABLE 5 CHEMICAL PROPERTIES OF EXTRACTED ATILI OIL

PROPERTY	VALUE
Saponification value	116.13
Acid Value	0.22
Free fatty acid	0.11
Ester value	115.92

This value is slightly lower than what was previously obtained by means of extracting with n-hexane (Nabage, 2010). The saponification value was also calculated as (116.127). This value compared favourably to values obtained by Agu, *et al* (2008) for refined atili oil. This result suggests, that not only does extraction take place but the oil extracted is also partly refined in the process. The Free fatty acid (FFA), which is a measure of the extent to which glycerine in the oil has been decomposed by lipase and other actions was calculated as 0.11. This suggests that the glycerine was decomposed to a lesser degree by extracting with aqueous biphase system. This makes a lot of sense as one of the advantages of this method (extraction with ABS) is that, the interfacial stress (at the interface between the two layers) is far lower (400 fold-less) than water-organic solvent systems causing less damage to the molecule to be extracted (McCabe, *et al*, 2005). The value obtained also suggests that oil obtained by this method is edible since the acid value is used as a general indication/criteria of the condition of edibility of oils (Agu, *et al*, 2008). Physically, the extracted atili oil was found to have a golden yellow colour which was in contrast to atili oil extracted by Agu, *et al*, (2008) and that used by Damilola, (2011). This colour change was due to the absorption of the colouring matter contained in the oil by the salt-rich phase. Figure 4 shows the relationship between salt concentration and the volume of the PEG-rich phase.

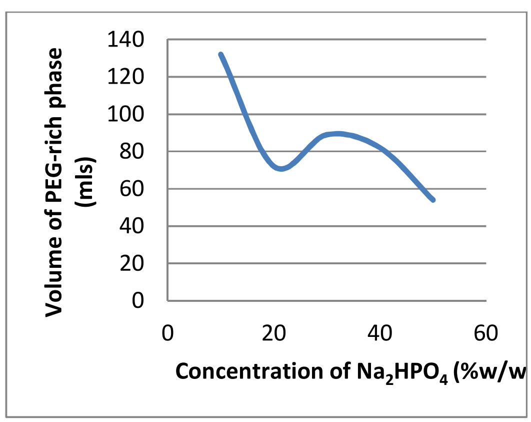

Figure 4 Effect of salt concentration on the extraction process.

It was noticed that an increase in salt concentration from 10%w/w to 20%w/w results in a slight decrease in the volume of the PEG-rich phase from 132mls to 72mls. This was as a result of the weak partition coefficient at 10%w/w resulting in the very little oil to PEG ratio in the upper phase. However, as concentration was increased from 20%w/w to 30%w/w, there was a slight increment in the volume of the PEG-rich phase before a steady decrease of the PEG-rich phase from this point if salt concentration is increased further. The behaviour of the graph around the salt concentration of 20%w/w and 30%w/w suggests the position of the optimum point for the extraction of atili oil using aqueous biphase system. Figure 5 shows the relationship between the varied concentration of salt and the yield of oil from the PEG-rich phase.

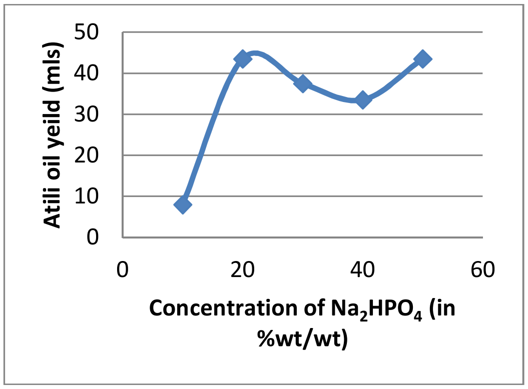

Figure 5 Effect of salt concentration on the yield of atili oil

At 10%w/w, only about 8mls of oil was recovered from the PEG-rich phase. However, as the concentration of the salt is increased to 20%w/w, the quantity of atili oil recovered from the PEG-rich phase increased sharply to 45mls, which suggests that the PEG-salt concentration (i.e. 40% PEG – 20% Na_2HPO_4) represents the optimum concentrations-combination and the most efficient system for this extraction.. This is consistent with previous findings (Liu, *et al*, 2011). Increasing the salt concentration beyond this point, results in the steady decline in the yield of oil from 45mls to 33.5 mls.

4.0 CONCLUSION

The following are the conclusions drawn from this work: Aqueous biphase systems can be used to extract atili oil. The combination of PEG-Na_2HPO_4 which offered the optimal yield of extracts is 40% PEG - 20%Na_2HPO_4. The effect of change in salt concentration is very sensitive from the point of view of the quantity of the PEG-rich phase. Atili oil extracted using aqueous biphase systems are edible. The atili oil extracted was also partly refined which makes it a cost effective method for commercial edible oil extraction.

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