Solid-liquid extraction of sorrel calyces with ethanol

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Abstract: Ethanol extraction of three particle size distributions of sorrel (*Hibiscus sabdariffa*) calyces was investigated. Extraction rate was found to increase with reduced particle size, increased temperature and solvent mass (solvent-feed ratio). At 30°C, maximum yield or concentration was achieved with 50:1 solvent-feed ratio but no substantial increment occurred in these parameters beyond 20:1 ratio. No degradation of the extract's components occurred between 27°C and 70°C since linear relation between extraction yield and temperature was sustained. Peleg equation and a variant of it gave the best fit for extraction kinetics. The smallest calyx particles (<2 mm) recorded the maximum (saturation) concentration (C_s) of 13.7103 g L^{-1}, the highest initial extraction rate (B_o) of 1.6510 g L^{-1} min^{-1} and the fastest time constant (τ_o) of 8.30 minutes while the analogous values for the biggest particles (2.8-5.6 mm) were 7.5162 g L^{-1}, 0.3401 g L^{-1} min^{-1} and 22.04 min.

Keywords: extraction kinetics, time constant, extract concentration, extraction yield, medicinal herbs

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1 Introduction

The ethanol extract of sorrel (*Hibiscus sabdariffa*) calyces has been found to be of medicinal value through scientific investigations (Mahadevan et al., 2009; Dahiru et al., 2003; Carvalal-Zarrabal et al., 2005; Carvalal-Zarrabal et al., 2009). Medicinal herbal products are usually presented either as liquid or powder after the bioactive components are extracted from vegetable plant source. Solid-liquid extraction process is influenced by the nature of the plant to be extracted, the solubility capacity, selectivity and viscosity of the leaching solvent and, the leaching conditions such as temperature, solvent volume or mass (i.e. solvent to feed ratio) and level of agitation among others (Richardson and Harker, 2002; Hanim, 1992; Olawale, 2012a, McCabe et al., 1984; Wijugaard and Brunton, 2010). It is thus obvious that the characteristics of both the solvent and the leached materials are important variables in solid-liquid extraction process.

The kinetics and equilibrium parameters are needed for design, optimization and operation of leaching equipment. A previous extraction study on sorrel calyces was carried out with water (Olawale, 2012a). Since the solubility capacity, selectivity, wetting ability and viscosity of ethanol are different from those of water, it is necessary to establish the kinetics and equilibrium parameters for ethanol extraction of sorrel calyces.

Some works have been reported on the solid-liquid extraction of oil, polyphenols and some other antioxidants, tannins and other useful vegetable plants' constituents (Olawale, 2012a; Olawale, 2012b; Wijugaard and Brunton, 2010; Mohamad et al., 2010; Simeonov et al., 2006; Jokicet al., 2010, Bucic-Kojic et al., 2007; Sayyar et al., 2009; Fikselova et al., 2008; Akinoso et al., 2006; Bera et al., 2006). Works on drying characteristics of sorrel (roselle) calyces were also reported (Saeed et al., 2008; Saeed, 2010); these studies would be useful in processing and utilization of roselle calyces. However, none of these works focused on ethanol extraction of sorrel calyces.

Therefore this research reports on the study of leaching of sorrel calyces with ethanol. The leaching

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was carried out on three different calyces' particles under varying conditions to obtain kinetic parameters.

2 Materials and method

2.1 Pretreatment of calyces

The calyces of sorrel (*Hibiscus sabdariffa*) used in this investigation were obtained from a local market in Nigeria and were dried at 40°C for 8 h. The dried calyces were reduced to the required sizes (with mortar and pestle) and then stored in air-tight polythene bags for subsequent uses.

Absorbance of the extracts (obtained by leaching the calyces with ethanol) was determined for various concentrations of the extract as already described (Olawale, 2012a). Correlation between the two variables was thereafter established for use in subsequent parts of the investigation.

2.2 Extraction of calyces with ethanol

Three particle size ranges of sorrel calyces were used for the leaching experiments. The particle size ranges were >2 mm, 2-2.8 mm and 2.8-5.6 mm, respectively. 1 g of each of these sorrel particle sizes was leached with a predetermined quantity of absolute ethanol to give the desired solvent to feed (calyces' particles) ratio under the conditions of temperature and time shown in Table 1.

Table 1 Variables used in ethanol extraction of sorrel calyces

Batch no.	Factor studied	Values for the factors		
		Temperature/°C	+S:F ratio	Time/min
1	+S: F ratio	60	1:5, 1:10, 1:20, 1:50	60
2	Temperature	27, 40, 50, 60	1:50	60
3	Time	60	1:50	15,30,45,60

Note: +S: F- Solvent to feed (solid) ratio.

The leaching experiments were carried out in a 250 mL round bottom flask in a thermo-stated water bath with thorough agitation. Three batches of leaching experiments were conducted with batches no. 1, 2 and 3 investigating the effects of solvent-feed (S:F) ratio, extraction temperature and leaching time respectively. The absorbance of the resulting extracts was determined after appropriate dilution and thereafter the concentrations of the extracts were obtained using Equation (1). The mass of the extracted components was obtained from the extract concentration data and extraction yields (Y_a) were subsequently evaluated with Equation (1). All experimental determinations were replicated.

$$Y_s = M_a \cdot 100 / M_s \quad (1)$$

where: M_s is the mass of the solid calyces leached.

3 Results and discussion

The deviations between data obtained from all replicated experiments were less than 1%. The ethanol extract concentration - C_t (g L^{-1}) - was correlated to absorbance (A) at 548 nm as (R^2 = 0.99): C = 1.499A

3.1 Effects of solvent mass (or volume) and temperature

Figure 1 presents the variation of extraction yield/extract concentration with solvent-solid mass ratio while yield and concentration changes with temperature are shown in Figures 2a and 2b.

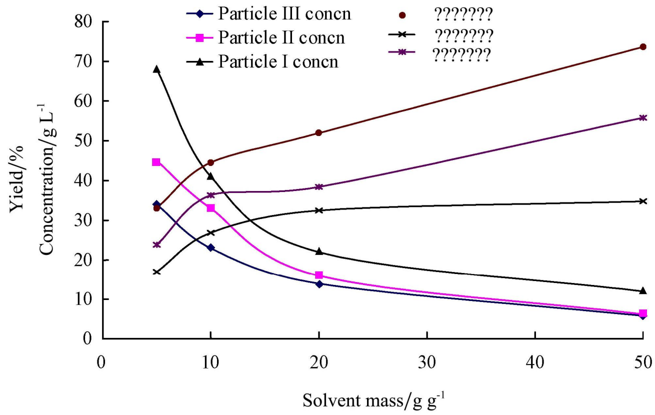


Figure 1 Yield/concentration variation with solvent mass for different particle sizes

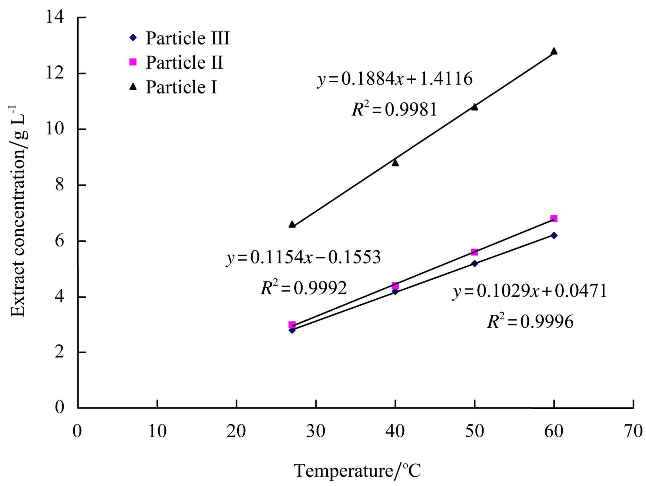


Figure 2a Extract concentration variation with temperature for different particle sizes

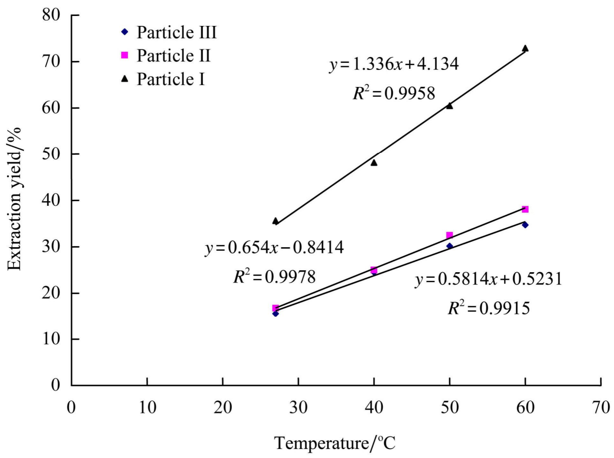


Figure 2b Extraction yield variation with temperature for different particle sizes

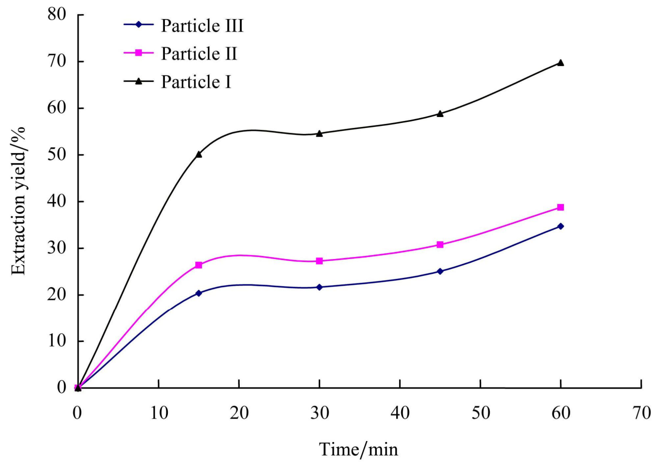
From Figure 1, it is seen that the extraction yield was highest with solvent-solid mass (S:F) ratio of 50:1 for the three particle sizes investigated. However, change in concentration and yield gradient was substantial only up to 20 g solvent/g solid. Nevertheless, for enhanced yield, solvent to feed ratio of 50:1 was chosen for the remaining parts of this investigation.

Figures 2a and 2b show linear increase of extract concentration and extraction yield with temperature. This was so because fluid viscosity usually decreases with the increasing temperature and reduced viscosity leads to increased diffusion rate and thus higher extraction rate (Richardson and Harker, 2002; Hanim, 1992; McCabe et al., 1984). The higher extraction rate would result in higher extract concentration, and extraction yield as long as thermal degradation of the desired components of the solid does not occur at the leaching temperature (Sayyar et al., 2009).

Extract concentration and extraction yield at a given temperature were observed to increase as the particle sizes of the sorrel calyces reduced since decreased particle size enhances diffusion rate (Richardson and Harker, 2002; Hanim, 1992; McCabe et al., 1984)

3.3 Solid-liquid extraction kinetics of sorrel calyces with absolute ethanol

From Figure 3 the extraction yield could be observed to vary with time in exponential decay fashion as expected of diffusion controlled process such as leaching and sorption (Richardson and Harker, 2002; Bucic-Kojic et al., 2007). This trend was also observed for change in extract concentration with time in this investigation. The highest extraction rate was observed to occur within the first twenty minutes of the leaching experiment. The initial rate appeared to increase as the particle size of calyces reduced.



Legend: Particle I - <2 mm; Particle II – 2-2.8 mm; Particle III – 2.8 – 5.6 mm

Figure 3 Extraction yield variation with time for different particle sizes

The kinetics of the extraction process was evaluated with DataFit 9 software. Assessment of fit statistics (i.e. R^2, SSE, RMSE) indicated Equation (2) and Equation (3) as the most appropriate, of all exponential decay equations in the software's database, to fit the leaching experimental data.

$$C_t = t/(K_1 + K_2 t) \tag{2}$$

$$C_t = K_1' t/(t + K_2') \tag{3}$$

The parameters and the fit statistics for Equations 2 and Equation (3) are given in Table 2. The extraction process parameters such as the maximum concentration (C_s), initial extraction rate (B_o) and time constant (τ_o) which are either given as the fit parameters or derived from these fit parameters (given in Table 2) are presented in Table 3.

Equation (2) is Peleg equation which is commonly used to model the kinetics of solid-liquid extraction process (Peleg, 1988; Jokic et al., 2010, Bucic-Kojic et al., 2007). It has been found appropriate for describing the kinetics of extract concentration; it is equally appropriate as the kinetic model of the extraction yield of sorrel calyces. Equation (2) and Equation (3) are hyperbola function and the latter could be reduced to Peleg equation.

The coefficient of determination (R^2) and adjusted R^2 were greater than 0.9 for the three particles as is shown in Table 2. This indicated the appropriateness of these equations for describing the ethanolic leaching of sorrel calyces, since the closer these values were to 1.0 the better. The other two fit statistics, RMSE and SSE, indicated accuracy and the nearer to zero their values, the better the accuracy.

Table 2 Parameters and fit statistics of extraction kinetic models for sorrel calyces

Particle	Equation	Parameters		Fit Statistics			
		K_1	K_2	R^2	Adj R^2	*SSE*	*RMSE*
I	Eq 2	0.6056	0.0729	0.9867	0.9807	0.13324	0.04442
	Eq 3	13.7102	8.3041	0.9867	0.9807	0.13324	0.04442
II	Eq 2	1.2175	0.1424	0.9624	0.9601	0.10018	0.03332
	Eq 3	7.0211	8.5484	0.9624	0.9601	0.10018	0.03332
III	Eq 2	2.9398	0.1330	0.9263	0.9242	0.15039	0.05013
	Eq 3	7.5162	22.0447	0.9914	0.9242	0.15039	0.05013

Note: R^2 – coefficient of determination; adj R^2- adjusted coefficient of determination; SSE – sum square of error; RMSE – root mean square of error. Particle I : <2 mm; Particle II: 2.0-2.8 mm; Particle III: 2.8-5.6 mm.

Table 3 Ethanol extraction process parameters of sorrel calyces

Parameters	Particle I	Particle II	Particle III
Maximum concentration (C_s)/g L^{-1}	13.7102	7.0211	7.5162
Initial extraction rate (B_o)/g $L^{-1}min^{-1}$	1.6510	0.8213	0.3401
Time constant (K'_2 or τ_o)/min	8.3041	8.5484	22.0447

The attraction of Equation (3) is that two important solid-liquid extraction/sorption process parameters – maximum yield, maximum concentration or capacity (C_s) and time constant or time to reach optimum extraction rate (τ_o) – are variables of the equation while the initial extraction or sorption rate (B_o) is obtained as the ratio of these two aforementioned parameters (Olawale, 2012a, 2012b).

From the values of these process parameters, it is seen that particle I (<2 mm) gave the highest maximum (saturated) extract concentration of 13.71 g L^{-1} (also the highest maximum yield) and highest initial rate of 1.651 g L^{-1} min^{-1}. It also recorded the fastest time constant of 8.30 min while the largest particles recorded the slowest time of 22.04 min.

4 Conclusion

Ethanol extraction of sorrel calyces recorded increased extraction rate with reduced particle size, increased temperature and ethanol volume. The kinetics of the liquid-solid extraction was fitted to two hyperbola functions, namely Peleg equation and a variant of it as was the case with water extraction of the calyces. The smallest of the three sorrel calyx particles gave the largest saturation extract concentration (C_s) and initial extraction rate (B_o) and, the fastest time constant (τ_o). There was no indication of degradation of sorrel calyces' bioactive components when extracted with ethanol between 27^0C and 70^0C.

Nomenclature

B_o, K'_1	initial extraction rate/g $L^{-1}min^{-1}$
C_s, K'_2	maximum extraction yield or concentration, (cg) g^{-1}
C_t	concentration, g L^{-1}
Eq.	equation
K_1	Peleg rate constant, g.min$(cg)^{-1}$
K_2	Peleg maximum capacity, g $(cg)^{-1}$
R^2	coefficient of determination
t	time/min
%	percent
τ_o	extraction time constant/min

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