Subcritical Water Hydrolysis Treatment of Waste Biomass for Nutrient Extraction

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Nutrients were extracted from corn stalks, peanut shells, de-oiled peanut meal, chicken manure, and sewage sludge by a subcritical water (SCW) hydrolysis reaction. Compared with the other feedstock, the aqueous phases extracted from de-oiled peanut meal showed the highest water-soluble organic carbon, amino acid, total nitrogen, and phosphorus contents. The effects of solution pH, final hydrothermal temperature, and reaction time on nutrient extraction from de-oiled peanut meal were investigated. The analysis showed that alkaline reagents promoted liquefaction. The highest yield of the total primary nutrients (82.6%) was obtained with extraction reaction at 180 °C for 1.5 h using 0.1 mol/L KOH. The liquid fraction from this reaction was investigated for its potential use as a fertilizer with germination experiments. A higher germination index and root activity were obtained using the liquid extract with the appropriate dilution. These results indicated that subcritical water hydrothermal treatment is a viable way to recover nutrients from biomass wastes. In addition, de-oiled peanut meal is a suitable feedstock for the production of nutrient-rich liquid extract.

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INTRODUCTION

Common biomass, including crop residues, animal manure, and industrial biomass by-products, amounts to more than 150 million tons annually (Darji *et al.* 2015). Furthermore, more than 30 million tons of sewage sludge is produced globally by municipal wastewater treatment plants, with an annual 2% increase in volume (Tu *et al.* 2014). Most of these biomass materials are discarded as waste, either in landfills or by incineration. Because of the high content of biodegradable organic components in biomass wastes, these disposal methods lead to severe environmental problems, including odor pollution, high-concentration of leachates, greenhouse gas emissions, and dioxin releases (from incineration) (Liu *et al.* 2012). Compared with the traditional methods, composting is a more promising solid biomass waste disposal strategy that converts biomass waste into solid fertilizer. This technology is widely used, but it has disadvantages, including a long residence time, odor release, and pathogen production (Simujide *et al.* 2013; Blazy *et al.* 2015). Therefore, the development of an alternative high-efficiency and environment-friendly method is welcomed.

A number of recent studies have demonstrated that water in subcritical conditions (100 °C < T < 374.2 °C) presents unique features with respect to its properties such as density, dielectric constant, ion concentration, diffusivity, and solubility. In subcritical water (SCW), organic materials are decomposed into smaller molecules through hydrolytic reactions (Liu *et al.* 2015). Hence, SCW has been developed for technologies that effectively convert organic waste into useful products. For example, SCW hydrolysis treatment had been applied in the production of bio-oils from oil palm fruit press fiber waste (Mazaheri *et al.* 2010), microalga (Duan and Savage 2011), oleaginous yeast (Tsigie *et al.* 2012), and oil palm empty fruit bunch (Ahmad Kurnin *et al.* 2016). Gaseous fuels such as hydrogen and methane, also can be produced from cellulose, lignocelluloses, and lignin-containing biomass materials by using subcritical hydrothermal treatment (Zhu *et al.* 2011). Furthermore, this technology is also effective for producing amino acids from protein-rich biomass feedstock, such as bovine serum albumin (Rogalinski *et al.* 2005), de-oiled rice bran (Sereewatthanawut *et al.* 2008), soybean meal (Watchararuji *et al.* 2008), fish waste (Zhu *et al.* 2008), and hog hair (Esteban *et al.* 2010). However, the complex components in gas and liquid extracts collected from the hydrothermal treatment require further purification and separation. Because biomass wastes are nutrient-rich natural resources (Pleissner *et al.* 2013), SCW hydrolysis treatment could simultaneously extract a variety nutrients from biomass wastes, and the liquid extract could be used as a fertilizer. Compared with composting, the SCW treatment process presents a relatively short reaction time, absence of any odor, and complete elimination of pathogens during the thermal conversion process. However, few previous studies have addressed the nutrient extraction from solid biomass wastes using SCW hydrolysis or the changes in nutrient value during the thermal treatment process.

In this study, SCW hydrothermal reactions were used to extract organic matter and macronutrients from biomass waste. Five biomass solid wastes were chosen, *i.e.*, corn stalks, peanut shells, de-oiled peanut meal, chicken manure, and sewage sludge. To achieve a nutrient rich aqueous phase and high extraction efficiency, different extraction conditions were tested, including initial solution pH, alkali agent, hydrothermal temperature, and reaction time.

The effects of these factors on the concentration of water-soluble organic carbon, amino acids, and macronutrient elements (N, P, and K), important for fertilizer, were evaluated. Furthermore, germination experiments were used to evaluate the resultant liquid residue as a potential liquid fertilizer.

EXPERIMENTAL

Materials

Five different biomass wastes were used as feedstocks. Dewatered sewage sludge was obtained from the Lie De municipal wastewater treatment plant in Guangzhou, China. Chicken manure, corn stalks, and peanut shells were obtained from Zhongluotan base farm in the Conghua District of Guangzhou, China. De-oiled peanut meal was collected from Jinlin peanut oil mill located in the Tianhe District of Guangzhou, China. All samples were dried at 70 °C for 72 h to achieve a constant weight. Subsequently, the samples were ground, sifted through an 80-mesh sieve, and stored in desiccators.

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Extraction of Nutrients

All experiments were carried out in a 100-mL Teflon-lined stainless-steel autoclave. For each test, 5 g of the biomass materials and 50 mL of deionized water were processed in an autoclave. Sealed autoclaves were put into a high temperature oven. When the oven reached the desired final hydrothermal temperature, the starting time was noted. The reaction temperature ranged between 120 and 200 °C in this study. After the desired reaction time (0.5 to 2.0 h), the reactor was cooled. The products were collected and passed through a 0.45-μm Millipore membrane filter. The water-soluble fraction was stored in a refrigerator (4 °C) for further analysis. The solid fraction was washed several times with deionized water and then dried at 70 °C until a constant weight was achieved. All experiments were repeated three times; the results are presented as the mean values with a relative standard deviation of less than 5%.

Analytical Methods

The pH and conductivity of the liquid samples were measured using a Sartorius PB-10 pH meter (Sartorius AG, Goettingen, Germany) and a DDS-11A conductivity meter (Shanghai Leici, Shanghai, China) at 25 °C. The total organic carbon (TOC) content in the solid sample and the water-soluble organic carbon (WSOC) concentration in the liquid samples were measured using an Analytik Jena Multi N/C 2100 TOC analyzer (Analytik Jena, of Jena, Germany). The extraction of WSOC in the aqueous phase collected after hydrothermal treatment was calculated using Eq. 1:

$$\text{Extraction rate of WSOC (\%)} = \frac{\text{The concentration of TOC in liquid residue} \times \text{the voulme of liquid}}{\text{The TOC of raw materials}} \times 100 \quad (1)$$

Amino acid content was detected using a photometric ninhydrin assay with L-glutamic acid as the standard (Sereewatthanawut *et al.* 2008). The H_2SO_4-H_2O_2 digestion method was used to pretreat solid and liquid samples prior to total nitrogen, phosphorus, and potassium content analysis. After digestion, the total nitrogen concentration (TN) of the liquid was determined using a Kjeltec TM 8200 Distillation Unit (Foss, Hillerød, Denmark). The total phosphorus content (TP) was analyzed using the molybdenum blue method at 700 nm on a Metash V-5000 spectrophotometer (Shanghai, China). Total potassium (TK) content was determined using a flame atomic absorption spectrophotometer (model ZA3300, Hitachi, Tokyo, Japan). The extraction of TN, TP, and TK was calculated using an equation similar to Eq. 1.

The amounts of cellulose and lignin in the raw biomass waste feedstock were analyzed following the traditional Van Soest detergent procedures (Hindrichsen *et al.* 2006). The biomass waste feedstock and freeze-dried liquid samples were mixed with KBr powder (1:100) to prepare the pellets for Fourier transform infrared (FTIR) spectroscopy analysis. FTIR spectra were recorded on a Bruker EQUINOX55 FT-IR spectrophotometer (Bruker GmbH, Karlsruhe, Germany) from 4000 to 400 cm^{-1}.

Germination Experiment

The liquid residue collected after hydrothermal treatment was tested as a culture medium for germination. Fifteen mung bean seeds were placed on Whatman #2 filter paper in each Petri dish. After variable dilutions with distilled water, 5 mL of each liquid was

pipetted into the Petri dish. Three replicates were analyzed for each diluted sample. In addition, a Petri dish was prepared using 5 mL of distilled water as a control. The germination experiment was conducted in a growth room at 27 °C. After 48 h, the germination rate was counted, and the root lengths were measured. The germination index (GI) was determined according to Eq. 2 (Huang *et al.* 2004).

$$\text{Germination Index (\%)} = \frac{\text{Seed gernination (\%)} \times \text{root lengthe of treatment}}{\text{Seed gernination (\%)} \times \text{root lengthe of control}} \times 100 \tag{2}$$

Root activity was measured using the triphenyl tetrazolium chloride (TTC) method (Liu *et al.* 2014).

RESULTS AND DISCUSSION

Composition of Raw Materials

The properties of raw biomass waste materials are shown in Table 1. The ash content of chicken manure and sewage sludge was 35.4% and 68.9%, respectively, which were much higher than that in corn stalks, peanut shells, or de-oiled peanut meal. The organic carbon content of chicken manure and sewage sludge was much lower than in the other three feedstocks. Higher weight percentage of cellulose and lignin were observed for corn stalks and peanut shells. De-oiled peanut meal presented the highest nitrogen content.

FTIR spectroscopy was used to analyze the composition of the raw biomass materials. The strong broad band around 3400 cm^{-1} was ascribed to –OH stretching vibrations of hydroxyl groups, and two intense absorbance peaks at 2926 cm^{-1} and 2864 cm^{-1} represented the –CH$_3$ and –CH$_2$ stretching vibrations, respectively, indicating the presence of carbohydrate or aliphatic compounds in all raw biomass materials (Sevilla and Fuertes 2009). Compared with the other three biomass wastes, chicken manure and de-oiled peanut meal spectra contained a peak at 3400 cm^{-1} that was shifted to a slightly lower wave position. This effect was attributed to N-H stretching in proteins or amino acids, which is consistent with the high nitrogen content in these materials (Table 1). Small stretching absorption bands at 1742 cm^{-1} were attributed to C=O vibrations in carbonyl, quinine, ester, or carboxyl groups. The strong band at 1635 cm^{-1} was ascribed to C=C stretching in olefinic or C=N stretching vibrations in the aromatic region (El-Hendawy 2006). The intense peak at 1470 cm^{-1} represented hydrogen-bonded carbonyl stretching and O–C–O stretching of the carbonate ion. For the corn stalks, peanut shells, and de-oiled peanut residues, overlapping bands at 1430 to 1420 cm^{-1} and 1250 cm^{-1} were observed, which were assigned to the finger print regions of lignin (–O–CH$_3$ deformation vibration) and hemicellulose (C–O stretching vibration) (Yang *et al.* 2007; Zhang *et al.* 2015). The absorbance peaks between 1200 cm^{-1} and 950 cm^{-1} included C-O stretching vibrations (1163 cm^{-1}) of esters and C-OH vibrations (1032 cm^{-1}) of carbohydrate. Furthermore, strong and asymmetrical peaks were observed for the chicken manure and sewage sludge at regions below 800 cm^{-1}, which were likely related to the high content of inorganic components (Marques *et al.* 2011). Generally, chicken manure and sewage sludge contained more carbonate salts and other inorganic components, while more lignin or hemicelluloses were detected in the other three materials. Furthermore, chicken manure and de-oiled peanut meal had a higher protein content.

Table 1. Properties of Raw Biomass Materials

Materials	Ash (wt.%)	Cellulose (wt.%)	Lignin (wt.%)	TOC (wt.%)	TN (wt.%)	TP (wt.%)	TK (wt.%)
Corn Stalks	5.3	30.1	14.8	48.96	0.75	0.16	2.24
Peanut Shells	1.8	16.9	26.4	49.99	2.25	0.10	0.64
De-Oiled Peanut Meal	5.9	12.8	14.3	46.02	9.43	0.88	1.30
Chicken Manure	35.4	9.5	7.6	28.46	3.34	1.77	2.75
Sewage Sludge	68.9	5.7	5.1	13.70	1.08	1.24	0.55
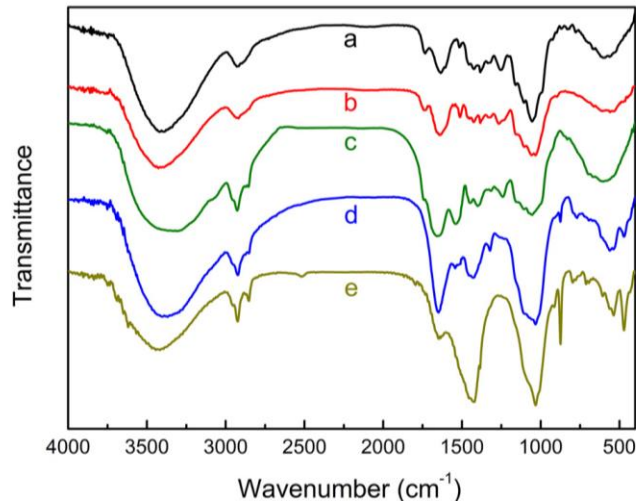
Fig. 1. FTIR spectra of raw materials: (a) corn stalks, (b) peanut shells, (c) de-oiled peanut meal, (d) chicken manure, and (e) sewage sludge

Nutrient Extraction from Biomass

Preliminary experiments were conducted using corn stalks, peanut shells, de-oiled peanut meal, chicken manure, and sewage sludge feedstocks.

Table 2. Physicochemical Properties of Liquid Residues from Different Materials

Materials	Volume (mL)	pH	EC[a] (ms/cm)	WSOC[b] (g/L)	TN (g/L)	AA-N[c] (mg/L)	TP (g/L)	TK (g/L)	Solid Residue (%)
Corn Stalks	36.2	3.38	2.0	15.69	0.32	24.1	0.12	1.88	54.0
Peanut Shell	36.9	4.02	1.6	10.48	2.15	28.4	0.05	0.24	77.2
De-Oiled Peanut Meal	38.2	5.04	6.8	30.17	6.58	1557.9	0.89	1.35	43.4
Chicken Manure	39.1	6.86	6.8	11.81	3.17	319.8	0.32	2.70	59.2
Sewage Sludge	45.0	6.94	4.6	4.97	0.63	117.2	0.02	0.15	81.6

[a] EC: Electrical conductivity; [b] WSOC: Water-soluble organic carbon; [c] AA-N: Amino acid nitrogen
Liquid-to-solid ratio: 10, Reaction temperature: 180 °C, Retention time: 2.0 h

After the five materials were treated with SCW hydrolysis, the concentrations of water-soluble organic carbon (WSOC), total nitrogen (TN), amino acid nitrogen (AA-N), total phosphorus (TP), and total potassium (TK) in the aqueous phases were analyzed (Table 2). The density of each collected liquid residue was higher than that of water, indicating that soluble components were extracted from the feedstock into the liquid phase by hydrothermal treatment. The aqueous phase solutions produced from corn stalks, peanut shells, and de-oiled peanut meal were acidic. Organic acids may have been released by the thermal reaction; during the hydrothermal process, cellulose, glucose, soluble protein, and amino acids are degraded to low molecular weight carboxylic acids (Quitain *et al.* 2002). Those acids include acetic acid, formic acid, propionic acid, succinic acid, lactic acid, *etc.*, and their dissociation constants (pK_a) are between 2.0 and 5.0. The liquid residue from chicken manure and sewage sludge was neutral, which could be due to their low organic matter content, or the high ash content could buffer the material during the hydrothermal process.

As presented in Fig. 2, the liquid sample obtained from de-oiled peanut meal was rich in organic carbon, nitrogen, amino acids, and phosphorus; the corresponding extraction rates for organic carbon, nitrogen, phosphorus and potassium were higher than 50% (ca 50.1, 53.3, 75.6 and 74.7%, respectively). Furthermore, the extraction efficiency of total primary nutrients, including total nitrogen, P_2O_5, and K_2O, was 60.2%. These results were attributed to the high content of carbohydrates, proteins and crude fats in the raw materials (Yadav *et al.* 2012). The total amino acid nitrogen (AA-N) in the liquid residues was as high as 1.56 mg/L for the de-oiled peanut meal, indicating that about 89 mg of amino acids was extracted per gram of dried de-oiled peanut meal. When de-oiled rice bran and de-oiled soybean were treated by SCW hydrolysis, the highest amino acid yield was 9.59 mg/g for de-oiled rice bran treated at 200 °C for 30 min and 20.67 mg/g for de-oiled rice bran treated at 210 °C for 30 min (Watchararuji *et al.* 2008). Taken together with these results, de-oiled peanut meal was chosen as the most suitable feedstock for a high yield of amino acids.
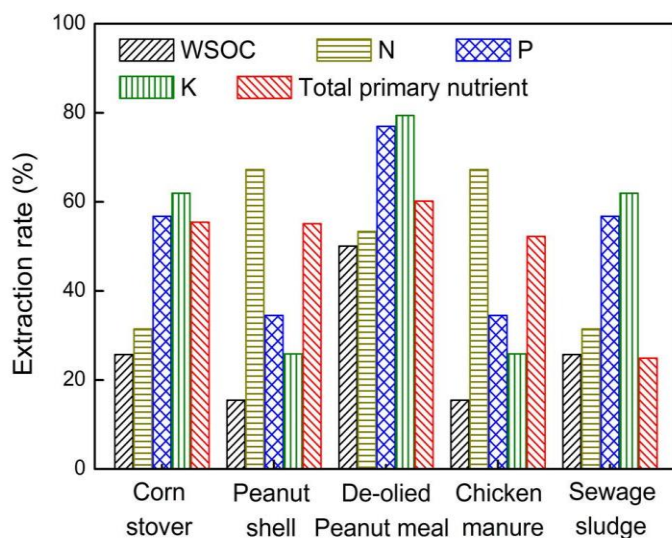

Fig. 2. Extraction of WSOC, TN, TP, TK, and total primary nutrients in liquid residue produced from SCW hydrolysis of different materials (Liquid-to-solid ratio: 10, reaction temperature: 180 ºC, retention time: 2.0 h)
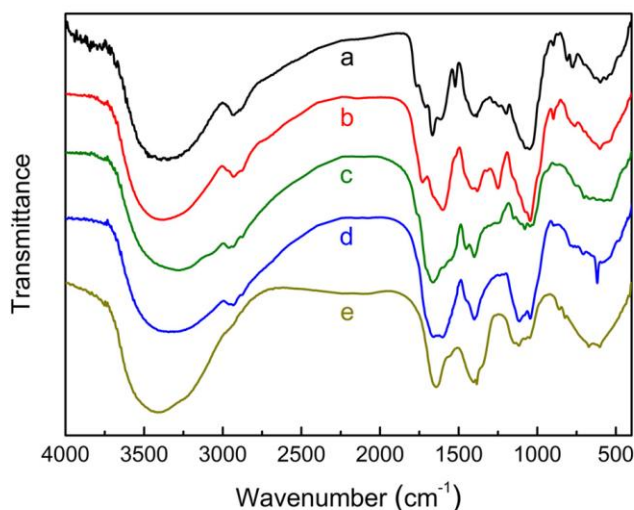
Fig. 3. FTIR spectra of liquid products obtained from the hydrothermal treatment of (a) corn stalks, (b) peanut shells, (c) de-oiled peanut meal, (d) chicken manure, and (e) sewage sludge

For comparison, an extraction experiment with water at ambient temperature and pressure was conducted with the de-oiled peanut meal feedstock. The concentration of WSOC, TN, TP, and TK in the water extracts was 6.39, 2.55, 0.08, and 0.33 g/L, respectively. The total yield of primary nutrients was 18.1%, which was about 1/3 of that obtained by the SCW hydrolysis treatment. These results demonstrated that SCW hydrolysis promoted the extraction of nutrients from raw biomass. Increasing the hydrolysis temperature from 25 °C to 180 °C increases water ionization content (K_w) from 1.01×10^{-14} to 3.5×10^{-12} (Bandura and Lvov 2006). The higher concentration of hydronium and hydroxide ions in the liquid phase enhances the hydrolysis reaction.

To reveal the main components in the liquid products produced *via* SCW hydrothermal treatment, FTIR analysis was carried out using the corresponding freeze-dried samples (Fig. 3). Compared with the raw materials, the stronger bands around 3400 cm^{-1} suggested higher carbohydrate content in the hydrothermal liquid residue, while a decrease in the intensity of the bands from 3000 to 2850 cm^{-1} represented a lower content of aliphatic compounds. The intense overlapping bands at 1750 to 1600 cm^{-1} were attributed to the C=O stretch of dimers in aromatic acid salts (El-Hendawy 2006), which may have formed during the hydrothermal reaction or subsequent freeze-drying. The strong carbonate ion band at 1470 cm^{-1} was not observed, but all samples contained bands with maximum peaks at 1380 cm^{-1}, which corresponded to NH$_4^+$ in inorganic compounds (Zhao *et al.* 2011). The peaks from 1250 to 1000 cm^{-1} represented the stretching of –OH bending vibration, C-O, C=O, and C-O-C stretching vibrations, suggesting that the samples were rich in polysaccharides (Gao *et al.* 2011).

Influence of the Experimental Conditions on the Nutrients Extraction

To maximize nutrient extraction, the most important operational variables of hydrothermal processing, including initial solution pH, reaction temperature, and retention time, and their influence on the fractionation of liquid residue were studied. Due to its relatively high extraction rate, the subsequent hydrolysis treatment experiments used de-oiled peanut meal.

Table 3. Liquid Residues Produced by SCW with Different Initial Solution pH

Treatment Condition	Initial pH	Volume (mL)	Final pH	EC (ms/cm)	WSOC (g/L)	TN (g/L)	TP (g/L)	TK (g/L)	Solid Residue (%)
0.1 mol/L H_2SO_4	0.70	36.0	2.91	8.87	26.27	7.37	0.88	1.40	49.6
0.005 mol/L H_2SO_4	2.00	37.5	4.89	6.56	27.14	6.91	0.87	1.34	45.2
Natural pH	6.82	38.2	5.04	6.84	30.17	6.58	0.89	1.35	43.4
0.01 mol/L NaOH	12.00	39.5	5.58	7.36	31.82	7.71	0.87	1.35	39.6
0.05 mol/L NaOH	12.70	42.3	7.15	8.82	32.24	8.45	0.72	1.35	34.8
0.1 mol/L NaOH	13.00	44.1	8.14	9.32	33.82	8.87	0.65	1.35	27.2
0.2 mol/L NaOH	13.30	45.1	8.40	11.77	34.48	8.83	0.48	1.34	27.0
Liquid-to-solid ratio=10, Reaction temperature: 180°C, Retention time: 2.0 h									

Effect of the initial solution pH

To investigate the influence of initial solution pH on nutrient extraction, the hydrolysis solution pH was adjusted with NaOH and H_2SO_4. The volume of liquid residue increased with increasing initial pH, while the weight of solid residue decreased (Table 3). Thus, alkali salts improved liquefaction yields and reduced the solid residue. Alkali salt is a common homogeneous catalyst used in hydrothermal processes to accelerate ionic reactions and promote glucose decomposition to water-soluble products (Muangrat *et al.* 2010). In this study, adding alkali salt to the system increased the concentration of soluble organic carbon and nitrogen in the liquid phase (Table 3). However, the TP concentration decreased when the initial solution pH was increased. The high concentration of hydroxide ions (OH⁻) in alkaline solution negatively affect the formation of PO_4^{3-} during hydrolysis.
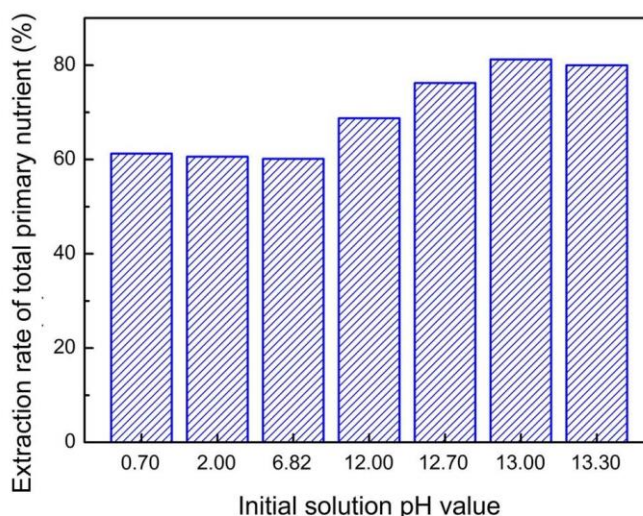

Fig. 4. Effect of initial solution pH on the extraction rate of total primary nutrients. Conditions: liquid-to-solid ratio: 10; reaction temperature, 180 °C; retention time, 2.0 h

The extraction rate of total primary nutrients in systems with different initial solution pH was calculated (Fig. 4). Extraction efficiency increased with increased NaOH

content, reaching a maximum value of 81.2% extraction with 0.1 mol/L NaOH (pH 13). However, the extraction rate did not increase with if the initial pH was higher than 13. Hence, the optimal NaOH concentration of 0.1 mol/L was used in subsequent experiments.

Influence of different alkaline reagents

Na_2CO_3, KOH, and K_2CO_3 alkaline reagents in concentrations of 0.05 mol/L, 0.1 mol/L, and 0.05 mol/L, respectively, were compared (Table 4). NaOH and KOH catalysts produced higher liquid residue volumes and solid mass conversion because of their stronger alkaline pH value compared with their corresponding carbonates. Sodium can produce some negative effects for soil properties and plant growth, while potassium is a plant nutrient (Tortosa *et al.* 2014). Considering the projected agricultural application of this process, KOH was chosen as the alkali extractant.

Akhtar *et al.* (2010) investigated the effect of alkalis (NaOH, K_2CO_3, and KOH) on the liquefaction of empty palm fruit bunch (EPFB) under subcritical water conditions; the reactivity of alkaline regents in decreasing order was K_2CO_3 > KOH > NaOH. The highest liquid hydrocarbon yield was obtained using the K_2CO_3 catalyst, as it enhances lignin degradation (Akhtar *et al.* 2010). This effect could explain the higher WSOC concentration for the liquid residue when 0.05 mol/L of K_2CO_3 was used (Table 4). When the extraction rate of total primary nutrients was calculated for the KOH and K_2CO_3 systems, the total primary nutrients in the de-oiled peanut meal and the addition of K (added as 50 mL 0.1 mol/L KOH or 50 mL 0.05 mol/L K_2CO_3) was both included in the theoretical value. The total primary nutrient extraction was 79.6% with KOH and 77.0% with K_2CO_3. Therefore, 0.1 mol/L KOH was chosen as the extracting agent for subsequent runs.

Tortosa *et al.* (2014) also demonstrated the positive effect of an alkali extraction agent on the solubilization of organic carbon and nutrients from two-phase olive mill waste composts. However, 1.0 mol/L of KOH was necessary to obtain the maximum extraction rate at 70 °C and ambient pressure for 24 h (Tortosa *et al.* 2014), suggesting that SCW hydrolysis requires a smaller amount of alkali extraction agent than common heating treatments.

Table 4. Liquid Residues Produced by SCW with Different Alkaline Regents

Treatment Condition	Initial pH	Volume (mL)	pH	EC (ms/cm)	WSOC (g/L)	TN (g/L)	TP (g/L)	TK (g/L)	Solid Residue (%)
0.1 mol/L NaOH	13.00	44.1	8.14	8.82	33.82	8.87	0.65	1.35	27.2
0.05 mol/L Na_2CO_3	11.27	42.3	7.96	8.17	33.62	8.23	0.73	1.36	32.6
0.1 mol/L KOH	13.01	43.8	8.10	8.26	36.24	8.79	0.69	4.76	28.8
0.05 mol/L K_2CO_3	11.67	42.4	8.12	8.63	36.89	8.63	0.70	4.87	33.6
Liquid-to-solid ratio=10, Reaction temperature: 180°C, Retention time: 2.0 h									

Influence of the hydrothermal temperature and retention time

Next, the influence of different reaction temperatures and times on reaction efficiency were studied by using de-oiled peanut meal as feedstock. The temperatures ranged between 120 and 200 °C, and the reaction time was varied from 0.5 to 2.5 h. The surface contour plots of concentration of WSOC and macronutrients in the produced liquid as a function of reaction temperature and time are shown in Fig. 5. A binary function model

was used to fit the experimental values. The obtained predictive equations for the concentration of WSOC, TN, TP, and TK are presented in Table 5. The coefficients of determination (R^2) indicated a high degree of fitting between the two investigated factors and the model.

Figure 5a shows an increase in WSOC concentration with increased reaction temperature and retention time, reaching a maximum value of 39.0 g/L at 187.1 °C and 1.35 h. However, a higher temperature and longer reaction time did not enhance WSOC exaction, as WSOC content slightly decreased at high temperature and with a longer time. This result demonstrated the combined effect of temperature and time of exposure. Sereewatthanawut *et al.* (2008) achieved similar results when using de-oiled rice bran as the raw material to extract protein and amino acids by SCW hydrolysis; WSOC in the liquid phase obtained at 220 °C for 30 min of hydrolysis was lower than that obtained at 200 °C (Sereewatthanawut *et al.* 2008). Some water-soluble components may have been converted to gas-phase components or water-insoluble solid residue through carbonization (Goto *et al.* 2014). Additionally, the solid residue weights were measured for all experiments, and the residue rate was calculated. Twenty-seven percent of the solid material was left in the autoclave after treatment at 180 °C for 2.0 h, while the rate increased to 31.8% after treatment at 200 °C for 2.0 h and 30.2% at 180 °C for 2.5 h. Thus, carbonization was enhanced under high-temperature and long-reaction-time conditions.

Table 5. Predictive Equations and Predicted Maximum Values

Predictive Equations	R^2	Max Value		
		X_{max}	Y_{max}	Z_{max}
$Z_1 = -62.0487 + 0.9206X + 21.7250Y - 0.0022X^2 - 2.8730Y^2 - 0.0750XY$	0.9734	187.1	1.35	39.030
$Z_2 = -11.8151 + 0.2271X + 3.5382Y - 6.5679*10^{-4}X^2 - 0.5491Y^2 - 0.0115XY$	0.8485	159.6	1.55	9.022
$Z_3 = 0.0338 + 0.0045X - 0.7229Y - 1.7230*10^{-5}X^2 + 0.2781Y^2 + 0.0046XY + 5.4761*10^{-6}YX^2 - 0.0019XY^2$	0.9247	200.0	1.99	0.650
$Z_4 = 3.7420 + 0.0061X + 0.2933Y - 1.0804*10^{-5}X^2 - 0.0551Y^2 - 3.2819*10^{-4}XY$	0.9253	200.0	2.06	4.771
$Z_5 = 580.2420 - 10.7218X - 58.2175Y + 0.07162X^2 + 20.3020Y^2 + 0.6576XY - 1.5450×10^{-4} X^3 - 3.8803Y^3 - 0.0529XY^2 - 0.0019YX^2$	0.8524	173.3	1.83	79.51
Z_1: WSOC; Z_2: TN; Z_3: TP; Z_4: TK; Z_5: Extraction rate of total primary nutrients; X: treatment temperature; Y: retention time.				

A similar trend was observed for TN concentration in the liquid phase. Increasing treatment temperature and holding time was beneficial for the extraction of nitrogen, and the highest value (9.03 g/L) was obtained at 159.6 °C for 1.55 h. After that point, the nitrogen content in the liquid residue decreased gradually, as previously observed (Ren *et al.* 2006). A similar decrease in the concentration of organic nitrogen dissolved from restaurant garbage was observed when the hydrothermal temperature and heating time was higher than 180 °C and the reaction time was 60 min (Ren *et al.* 2006). These results could be explained by the hydrolysis reactions of protein and amino acid. During heating, the peptide chain is broken down, and the protein is hydrolyzed into smaller soluble molecules, such as multipeptides, oligomeric peptides, and amino acids. Higher treatment temperatures and longer retention times hydrolyze the amino acids to organic acids, NH_4^+, and CO_2 (Ren *et al.* 2006; Cheng *et al.* 2008). In the present study, some NH_4^+ would

transfer to the gaseous phase because of the presence of KOH, which leads to a decrease of TN in the extractant. To avoid nitrogen loss, the operation should be carried out at a mild temperature and with a short reaction time.
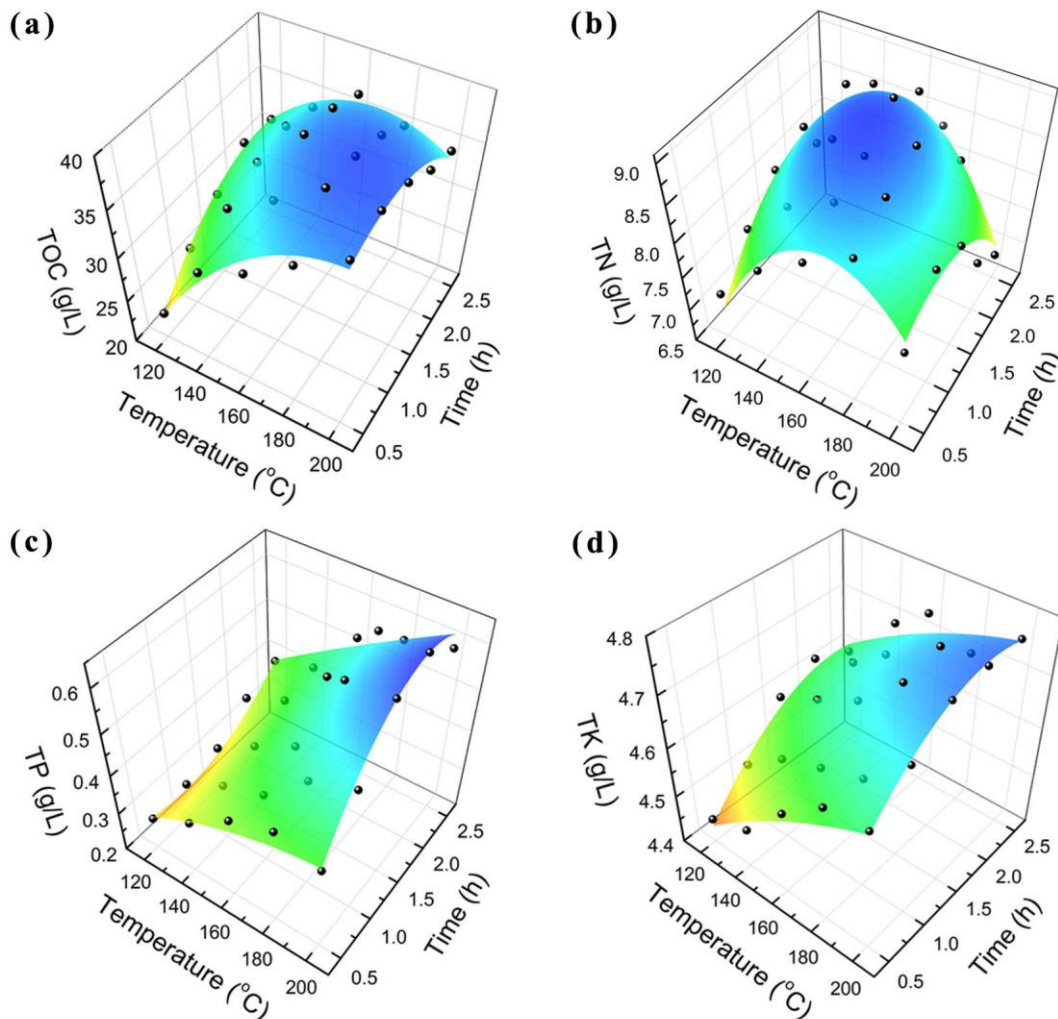

Fig. 5. Surface contour plots of the effects of hydrolysis temperature and retention time on the concentration of WSOC (a), TN (b), TP (c), and TK (d) in the liquid residue

For TP and TK, the concentration increased with hydrolysis temperature and treatment period gradually, reaching a platform when the temperature was above 180 °C and retention time was longer than 2 h (Fig. 5a and d). With increasing temperature and retention time, the water extracted more P and K, which could not be extracted at lower temperatures and shorter time periods. According to the predictive equations, the maximum value of TP and TN appeared at 200 °C and 1.99 h and 200 °C and 2.06 h, respectively.

The experimental results indicated that the most effective hydrothermal treatment conditions were 180 °C and 1.5 h for recovering nutrients from de-oiled peanut meal. (Fig. 6). Under these conditions, 82.6% of total primary nutrients were extracted, suggesting that most nutrients in the original de-oiled peanut meal were recovered in the soluble product. The statistically predicted optimal conditions for the highest extraction rate of total primary nutrients (79.5%) were 173.3 °C and 1.83 h (Table 5). A discrepancy between the experimental results and the statistically predicted values was observed, indicating that the

extraction rate of total primary nutrients gotten after calculation may cant fitted well by multi-order functions with treatment temperature and reaction time as independent variables.
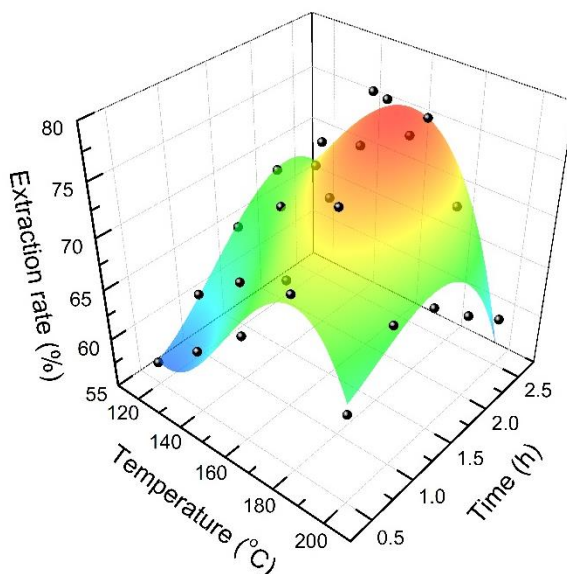

Fig. 6. Extraction rates of total primary nutrients for the liquid residue obtained from de-oiled peanut meal by SCW hydrolysis treatment under different hydrolysis temperatures and retention times

Germination experiment

The liquid product obtained from de-oiled peanut meal after treated at 180 °C for 1.5 h was tested as a culture medium for the germination experiment (Table 6).

Table 6. Germination Experiments

Dilution	0×	50×	100×	200×	500×	1000×	2000×	5000×	Distilled Water
Germination Rate (%)	86.7	91.1	95.6	100.0	100.0	100.0	100.0	97.8	97.8
Average Root Length (mm)	5.4	32.1	32.9	32.6	36.0	29.6	27.8	30.6	29.5
Germination Index (GI)	16.1	101.4	108.9	113.1	124.8	102.6	96.4	103.5	-
Root Activity (mg TTF/(g•h))	1.104	1.147	1.152	1.157	1.196	1.245	1.279	1.293	1.132

The undiluted liquid residue showed the lowest germination index (GI) and root activity, indicating that too much concentrated liquid residue negatively affected germination. After dilution, the GI and root activity increased dramatically and were higher than when the root was germinated in distilled water. Although the nutrient content in the liquid extract was low compared with commercial liquid fertilizer, it could be used as a liquid fertilizer after the addition of supplemental nutrients. These results indicated that SCW hydrolysis is an efficient process for recovering nutrients from biomass wastes.

CONCLUSIONS

1. De-oiled peanut meal is an optimal feedstock because of its nutrient-rich properties and high nutrient extraction rate.

2. Nutrient extraction and operational conditions (initial solution pH, hydrothermal temperature, and retention time) are closely related. Alkaline regents promoted nutrient extraction during SCW hydrolysis. Furthermore, increased reaction temperature and retention time generated higher amounts of water-soluble organic carbon (WSOC), nitrogen (TN), phosphorus (TP), and potassium (TK) in the liquid phase, with a maximum value at a certain temperature. However, with further increases in temperature and treatment time, WSOC and TN decomposed.

3. The optimal conditions for nutrient extraction from de-oiled peanut meal are a temperature of 180 °C, retention time of 1.5 h, and 0.1 mol/L of KOH as the extracting agent. Under optimized conditions, the extraction of total primary nutrients reaches 82.6%.

4. The nutrient-rich liquid residue from subcritical water hydrolysis of waste biomass is a beneficial medium for seed germination.

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