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ORIGINAL RESEARCH

The effect of water, urea, sodium hydroxide, and hydrogen peroxide processing on the cumin residues animal digestibility

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Abstract

Purpose No research has been published on the effect of chemical processing on the degradability and nutritional value of cumin residue. Chemical processing, such as urea, sodium hydroxide, and hydrogen peroxide, has been widely investigated to increase the nutritional value of grain residues, but information on cumin residue is limited. The effects of untreated and treated (water, sodium hydroxide, urea, and alkaline hydrogen peroxide) cumin residue on the ruminal digestibility and chemical composition were investigated in this study.

Method After treating cumin residues with the abovementioned chemical compounds, the chemical composition was evaluated with the standard procedures. Batch culture and gas production procedures were used to test the digestibility and gas production of treated and untreated cumin residue.

Results The chemical compositions of cumin residues were significantly altered by chemical treatments ($P < 0.05$). Processing cumin residues with urea, hydrogen peroxide, and sodium hydroxide reduced the dry matter (DM) compared to the control treatment ($P < 0.01$). Processing cumin residues with sodium hydroxide significantly reduced DM digestibility compared to the control. The highest levels of DM digestibility and microbial mass production were also found in water treatment. Urea treatment increased the yield of microbial mass-produced compared to other treatments ($P < 0.01$).

Conclusion In general, water and urea treatments increased the cumin residue digestibility more than other treatments, but sodium hydroxide and hydrogen peroxide treatments did not increase the cumin residue digestibility as expected.

Keywords Urea, Sodium hydroxide, Hydrogen peroxide, Chemical composition, Digestibility, Cumin residues

Introduction

Production of high-quality forages such as alfalfa hay and corn silage demand a large amount of land and water, both of which are limited in many places worldwide. As a result, by-product feeds and agricultural residues are commonly used as fiber sources in dairy cow rations (Kahyani et al. 2019). Agricultural by-products are increasingly being used in animal nutrition, because they may decrease feeding costs, among other reasons that are equally or even more significant (Marcos et al. 2020). Straw consumption varies depending on how it is processed, produced, and fed to the animals. Chemical, physical, and microbiological treatments enhance the animal's straw intake (Aquino et al. 2020). While straw

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is rich in cellulose and hemicellulose, ruminants have difficulty digesting it because of lignin and silica, therefore animals only have access to limited amounts of it (Ahmed et al. 2002). It may be needed to improve the agricultural residual quality to increase the efficiency of utilization by the digestive tract of ruminants (Mirzakhani et al. 2021).

Cumin, with 25,000 hectares, is the first area under cultivation of Iranian medicinal plants. Cumin is one of history's most respected medicinal seeds, available in black and green varieties. The nutritional value and biological activity of cumin seed (black or green) have been widely investigated (Srinivasan 2018; Yimer et al. 2019; Kulyar et al. 2021; Sarkar et al. 2021). Cumin is a commercially important seed spice recognized for its aroma and medicinal and therapeutic effects. Cumin has been found to have anticancer, antidiabetic, antiradical, and immunomodulatory properties, as well as being analgesic, antibacterial, anti-inflammatory, bronchodilator, spasmolytic, antihypertensive, hepatoprotective, and renal protective characteristics (Ramadan 2007). For decades, cumin seeds have been utilized to improve health and prevent diseases, particularly in Southeast Asia and the Middle East. However, according to our knowledge, no study has been conducted on the use of cumin residue as animal feed.

Agricultural by-products such as cumin residue can be used as ruminant feed, especially when conventional forages are limited. Biological and chemical treatments could increase the value of the agricultural by-product, which is poor in palatability, digestibility, and protein level, and thus in nutritional value (Suksombat 2004). Sodium hydroxide, ammonia, and urea are three substances that have been utilized to improve straw palatability, and digestibility (Aquino et al. 2020). These chemicals work by breaking the connections between the straw's lignin-cellulose structures, which are sensitive to alkaline or acidic conditions. Sodium hydroxide and other alkaline chemicals are absorbed into the cell wall of the straw during processing and react with the lingo-cellulosic components to damage the ester bonds between lignin, cellulose, and hemicellulose. The structural fibers enlarge due to the alkali absorbed into the straw, enabling microbial fermentation to proceed (Aquino et al. 2020). Wheat straw alkali processing has been shown to enhance cellulose and hemicellulose digestibility and availability, as well as nitrogen content (Haddad et al. 1994). Sodium hydroxide and urea increased rice straw gas production 48 hours after incubation (Liu et al. 2002). This procedure improves ruminal and total-tract fiber digestion and rumen microbial energy availability (Mirzakhani et al. 2021). In an *in vivo* study, it also has been shown that cows fed diets that contained up to 20% alkali-treated wheat straw performed similarly to cows fed diets that contained only alfalfa-haylage (Haddad et al. 1998).

To our knowledge, no study has investigated the effect of alkali processing on the nutritional value and chemical composition of cumin residues. We hypothesized that processing cumin residues with urea, hydrogen peroxide, or sodium hydroxide might improve fiber digestibility and fermentation characteristics. Thus, this study attempted to evaluate the effects of treating cumin residues with water, urea, hydrogen peroxide, or sodium hydroxide on chemical composition, mineral content, digestibility, and fermentation characteristics.

Materials and methods

Chemicals and treatments

Cumin residues were collected and crushed from Maraveh Tappeh fields before being transferred to Gonbad Kavous University for processing. The location of the area is shown in Fig. 1.

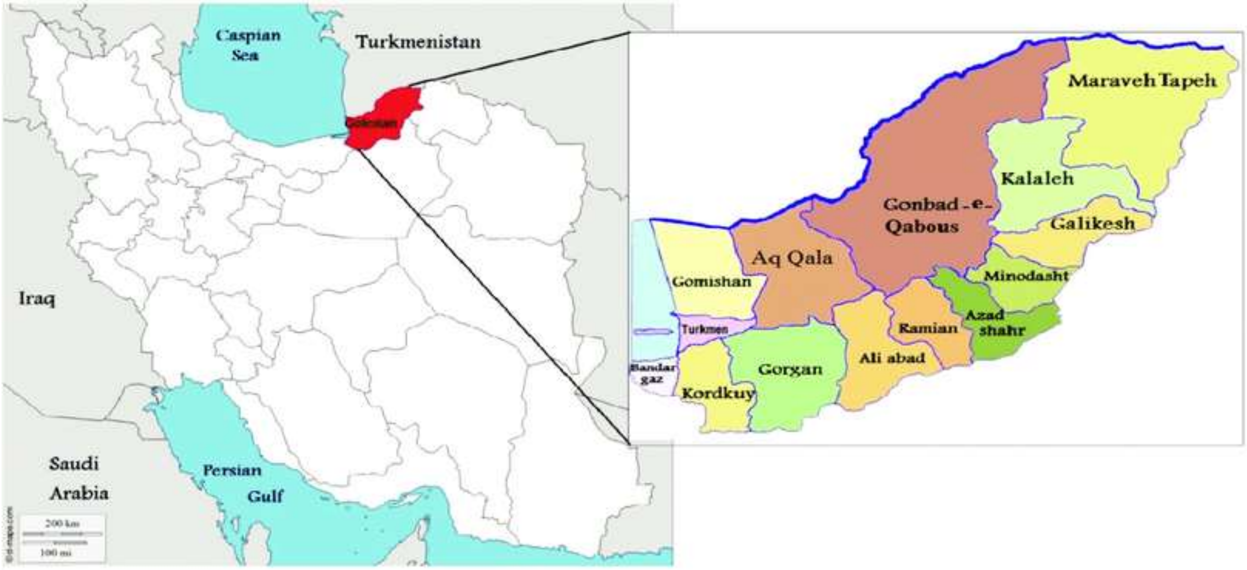

Fig. 1 A map showing the region where cumin was harvested

Unprocessed (control) cumin residues were compared to those treated with water, urea, sodium hydroxide, and hydrogen peroxide. Each treatment was applied on kg^{-1} cumin residue dry matter (DM) basis as described below: Two kg of cumin residue was combined with 5 liters of water for water treatment. The residues were then kept for 24 hours in plastic bags under anaerobic conditions. Sodium hydroxide (50 g) was dissolved in one liter of distilled water and sprayed on one kilogram of cumin residues DM for sodium hydroxide treatment. The materials were well mixed before being put into two-layer plastic bags and pressed. The bags were kept under anaerobic conditions for 72 hours (Chaudhry 2000). Cumin residues were first processed with sodium hydroxide before being treated with hydrogen peroxide. For this purpose, 100 g sodium hydroxide was dissolved in 0.5 liters of water, then added to 4 liters of water containing 2 kg cumin residue. Half an hour later, 114 ml of 35% hydrogen peroxide was dissolved in 0.5 liter of water and added to the mixture. The material was then well mixed and kept in plastic bags for 18 days in anaerobic conditions. The bags were opened and air-dried when the processing period was completed. The straw was treated using 1.5% sodium hydroxide w/w for 24 h in a container. After rinsing with cold water, the treated straw was tested for *in vitro* digestibility. For urea processing, 70 g of urea was first dissolved in 0.5 liters of water. Two kg of cumin residue and 4.5 liters of water were mixed adequately by hand, and the urea solution was added while mixing (García-Martínez et al. 2009). The prepared mixture was poured into two-layer plastics and compressed well.

Chemical analysis

The chemical composition of each sample was determined using five replicates. Proximate analysis was used to estimate DM, crude protein (CP), and ash (AOAC 2005). Standard methods were used to measure ADF and NDF (Van Soest et al. 1991). Equations No. 1, 2, and 3 were used to calculate growth net energy (NE_g), lactation net energy (NE_l), and total digestible nutrients (TDN; NRC 2001).

(1) $NE_g = (0.029 \times TDN) - 1.01$

(2) $NE_l = (0.0245 \times TDN) - 0.12$

(3) $TDN = (CP \times 0.36) - (ADF \times 0.77) + 81.38$

A flow meter was used to measure sodium and potassium, and a spectrophotometer (Biochrom Libera-S22) was used to detect magnesium, chloride, calcium, and phosphorus.

In vitro gas production assay

In the *in vitro* gas production experiment, untreated cumin residue (control) and treated cumin residue with water, urea, sodium hydroxide, and hydrogen peroxide were utilized as substrates. Menke's (1988) approach was used to conduct the gas production experiment. Before morning feeding, rumen fluid was obtained from three male Dalagh sheep (45± 2.5 kg) with ruminal fistulas. The animals were fed 30% concentrates (bran, barley, cottonseed meal, and supplement) and 70% forage diet (equal parts of corn silage and alfalfa). Water was available to the animals without restriction.

Artificial saliva and rumen fluid were mixed in a 2:1 ratio (2 volumes of artificial saliva and 1 volume of ruminal fluid). This mixture was then divided into 30 mL bottles containing 0.2 g processed or control samples. Each bottle was immediately bubbled for 10 seconds with carbon dioxide before being covered adequately with rubber stoppers and an aluminum lid. The bottles were incubated for 2, 4, 6, 8, 12, 24, 36, 48, 72, and 96 hours in a shaking water bath at 39 ºC. The cumulative gas and gas production parameters were estimated according to Orskov and McDonald's method (equation No. 4; Ørskov and McDonald 1979).

(4) $y = b\,(1 - e^{-ct})$

Where: y: the amount of gas production during the incubation time b: gas production from the fermentable insoluble fraction e: Euler's number c: rates of gas production for b portion t: time of incubation. The organic matter digestibility (OMD), metabolizable energy (ME), and net energy (NE) contents were calculated based on equations No. 5, 6, and 7 (Makar 2004; Menke et al. 1979).

(5) $\text{OMD}\ (\%) = 0.889\ \text{GP} + 14.88 + 0.0651\ \text{XA} + 0.45\ \text{CP}$

(6) $\text{SCFA}\ (\text{mmol}) = 0.0222\ \text{GP} - 0.00425$

(7) $\text{ME}\ (\text{MJ/kgDM}) = 0.136\ \text{GP} + 2.20 + 0.0029\ \text{CF} + 0.057\ \text{CP}$

Where: OMD: digestibility of organic matter SCFA: short-chain fatty acids ME: metabolizable energy GP: Net gas production after 24 hours (per 200 mg sample DM) XA: ash (%) CF: crude fiber (%) CP: crude protein (%). The SAS statistical program (version 9.1) analyzed the data in a completely randomized design (SAS 2003). The least significant difference (LSD) test was used to compare the means.

DM and OM digestibility

This test was similar to the gas production experiment in terms of rumen fluid processing, basal diet, and treatments. The batch culture technique was used to determine the *in vitro* digestibility of DM and OM (Theodorou et al. 1994). First, samples (500 mgDM) were placed in glass vials. Each vial was then filled with a 50 mL combination of ruminal fluid, and artificial saliva (one volume of ruminal fluid and two volumes of artificial saliva). The pH was then raised to 6.8 with the help of a buffer. The vials were put for 24 hours in a 39 °C water bath after being sealed with a plastic lid and aluminum cover. Then, the bottles were put in cold water at the end of the incubation time to inactivate the microbial activity. A pH meter was used to determine the pH (Metrohm Company, Model 691). The vial's contents were passed through a polyester cloth with a 42-mm pore size to remove undigested particles from liquid form. The liquid phase (5 mL) was combined with an equal amount of 0.2 N hydrochloric acids and kept refrigerated at -20 °C, to determine the ammonia nitrogen content. The ammonia nitrogen content was determined using the phenol-hypochlorite technique (Broderick and Kang 1980). The optical absorbance at 630 nm was measured using a spectrophotometer (Biotech-novaapec-England). The DM disappearance was determined by drying the undigested parts of the bottles after 48 hours in a 60 °C oven. The residual DM was then heated for six hours at 540°C, and the ash concentration was determined. At 2, 4, 6, 8, 10, 12, and 24 hours of incubation, gas pressure was measured by a pressure indicator, and the collected gas was released. The efficiency of gas production was calculated using equation No. 8 (Getachew et al. 2004).

(8) $G_y = GP_{24} / (0.5\text{- DM weight after drying in the oven})$

Where:

G_y = Efficiency of Gas Production

GP_{24} = The gas produced after 24 hours of incubation

The following equation was used to calculate microbial mass production (Blümmel et al. 1997b).

$MCP\ (mg) = (PF \times GP) - 2.2$

Where:

MCP= Microbial mass production

PF= Partitioning factor (mg of digested OM/mL of gas production)

GP= pure produced gas after 24 h (mL)

The following equation was used to calculate microbial protein efficiency:

The efficiency of microbial mass production = MCP/disappeared OM.

A completely randomized design was used to analyze the data using the GLM procedure of SAS statistical software version 9.1 (SAS 2003).

Results and discussion

Chemical composition

Chemical processing had a significant effect on chemical components (DM, ash, ADF, CP, TDN, NE_l, and NE_g; $P< 0.05$), except for NDF ($P= 0.089$; Table 1). In comparison to the control and water treatments, the utilization of urea, hydrogen peroxide, and sodium hydroxide resulted in a significant reduction in cumin residue DM. The cumin residue ash content was significantly increased after treatment with hydrogen peroxide, and NDF increased significantly after urea treatment. Hydrogen peroxide treatment decreased ADF compared to the control, whereas sodium hydroxide treatment significantly increased it. ($P< 0.05$). The urea treatment had the highest concentration (11.14%), whereas the sodium hydroxide treatment had the lowest concentration of CP (6.5%). Hydrogen peroxide treatment significantly increased the cumin residue TDN as compared to the control. Processing cumin residues with sodium hydroxide also reduced TDN, NE_l, and NE_g compared to the control and water treatments ($P<0.05$).

Cumin residues' Mg and Cl concentrations were unaffected by chemical treatments. Sodium hydroxide treatment reduced calcium, phosphorous, and sodium contents in cumin residue, while hydrogen peroxide treatment increased these minerals compared to other treatments ($P< 0.01$; Table 2). The sodium hydroxide treatment (92.35 mg/kgDM) also reduced potassium levels compared to the control (108.80).

Cumin residues DM decreased by all chemical treatments (Table 1). DM reduction in cereal straws due to chemical processing has been reported in other studies (Suksombat 2004). Similarly, processing wheat straw (Ribeiro et al. 2020; Dehghani et al. 2021) and rice straw (Aquino et al. 2020) with urea reduced DM. On the other hand, the treatment of agricultural by-products with urea and sodium hydroxide did not affect their DM content (Moura et al. 2020).

Table 1 Effects of chemical processing methods on the chemical composition and energy content of cumin residual

Treatments	DM (%)	NDF (%)	ADF (%)	CP (%)	TDN (%)	NE_L (Mj/Kg)	NE_g (Mj/Kg)
Control	94.54^{a}	74.10^{b}	46.52^{bc}	7.81^{bc}	48.37^{ab}	1.065^{ab}	0.392^{ab}
Water	94.37^{ab}	81.21^{ab}	49.10^{b}	8.77^{b}	46.72^{b}	1.025^{b}	0.345^{b}
Urea	93.83^{bc}	85.52^{a}	48.05^{b}	11.14^{a}	48.39^{b}	1.065^{ab}	0.392^{ab}
H_2O_2	93.2	71.46^{b}	41.01^{c}	8.20^{b}	52.89^{a}	1.17^{a}	0.523^{a}
NaOH	92.87	82.37^{ab}	57.2^{a}	6.5^{c}	39.68^{c}	0.85^{c}	0.145^{c}
SEM	0.187	3.04	1.76	0.418	1.41	0.036	0.0411
P-Value	0.0055	0.089	0.0109	0.0044	0.0098	0.0118	0.0099

DM: Dry matter; NDF: Neutral detergent fiber; ADF: Acid detergent fiber; CP: Crude protein; TDN: Total digestible nutrients; NEL: Net energy for lactating; NEg: Net energy for growth; SEM: Standard error of the mean.
a,b. Within the column, means with common superscripts do not differ (P> 0.05).

Table 2 Effects of chemical processing methods on the mineral content of cumin residual

Treatments	Ash (%)	Ca (mg/kg DM)	Mg (mg/kg DM)	P (mg/kg DM)	Na (mg/kg DM)	K (mg/kg DM)	Cl (mg/kg DM)
Control	9.54^{a}	10.60^{b}	4.15	0.225^{b}	150^{b}	108.80^{a}	16
Water	9.69^{a}	10.70^{b}	4.80	0.200^{bc}	144^{b}	101.35^{ab}	14.75
Urea	9.93^{a}	10.70^{b}	6.85	0.210^{bc}	144^{b}	99.60^{ab}	15.00
H_2O_2	17.87^{b}	13.10^{a}	6.25	0.290^{a}	179^{a}	110.70^{a}	16.15
NaOH	10.77^{a}	7.75^{c}	4.85	0.160^{c}	140^{b}	92.35^{b}	15.50
SEM	0.896	0.017	1	0.016	3.82	3.11	0.466
P-Value	0.005	0.0069	0.394	0.018	0.0037	0.0408	0.283

$^{a,b.}$ Within the column, means with common superscripts do not differ (P> 0.05).

Reduction in DM content can be attributed to dissolving water-soluble substances when sodium hydroxide, urea, and hydrogen peroxide were added.

The addition of hydrogen peroxide to cumin residue decreased the ADF concentration, whereas urea treatment raised NDF, and sodium hydroxide treatment increased ADF in the present study. Although no studies on cumin residues have been conducted, studies on other crop residues demonstrated that sodium hydroxide and hydrogen peroxide can decrease fiber content. Similarly, the ammonia treatment increased rice straw ADF content from 303 to 327 g/kg (Selim et al. 2004). Chemical processing has also resulted in increased ADF in bean residues (Alaei et al. 2019), consistent with our findings. In contrast, rice straw and bagasse NDF and ADF decreased following sodium hydroxide treatments, but not after urea treatments (Suksombat 2004). Urea treatments also reduced the NDF and hemicellulose levels of rice straw (Fadel Elseed et al. 2003). CaO treatment decreased the NDF content of barley straw by 11.4% (75.6 versus 64.2%) in *in vitro* research (Stehr 2019). On the other hand, sodium hydroxide did not reduce NDF and ADF contents in agricultural by-products (Bayat Kohsar et al. 2021). Alaei et al. (2019) also found that treating bean crop residue with water, sodium hydroxide, and hydrogen peroxide did not affect NDF concentration.

Chemical treatments improve digestibility by increasing lignin solubility or breaking the links between phenolic groups, lignin, and other cell wall components, especially hemicellulose. Extreme pH levels (above 8 or below 4) improve the solubility of hemicelluloses, making them more soluble (Suksombat 2004). As a result, alkaline chemical treatments can break the ester bonds between lignin, hemicellulose, and cellulose. These changes make it easier for rumen microbes to attack structural carbohydrates, enabling further degradation (Moura et al. 2020). The decrease in the cumin residue NDF content with hydrogen peroxide can be attributed to reducing lignin-hemicellulose ester bonds (Moura et al. 2020). Moura et al. (2020) demonstrated that treatments with either urea or sodium hydroxide at 60 g/kgDM resulted in reduced NDF and ADF content of the acerola fruit residue, while the concentration of 20 g/kgDM had no effect. Only the hydrogen peroxide treatment appears to have achieved these circumstances in our study.

Urea and sodium hydroxide treatments increased and decreased the CP content of the cumin residue, respectively ($P < 0.01$; almost 4%). Increases in CP were similar to those reported for urea-treated rice straw (Fadel Elseed et al. 2003; Suksombat 2004) and acerola fruit residue (Moura et al. 2020). Beauchemin et al. (2019) also reported that alkaline-urea treatment increased the CP of wheat straw from 2.5% to 10.3%. The ammonia treatment enhanced the N content in rice straw from 8.16 to 18.4 g/kg (CP content increased from 51 to 115 g/kg) (Selim et al. 2004). Urea is the most functional and frequently used chemical for processing agricultural by-products. Urea's main function is to improve the protein concentration of processed grain residue during the fermentation treatment (Aquino et al. 2020). This is because urea may bind to the straw and generate additional nitrogenous chemicals like acetamide (Ribeiro et al. 2020). The high protein equivalent of urea can explain the increase in CP concentration as urea was added. Conversely, it has been reported that adding calcium oxide, hydrogen peroxide, and sodium hydroxide to bean residues reduced CP (Alaei et al. 2019). CP concentration was also unaffected by sodium hydroxide treatment of agricultural waste (Moura et al. 2020). Decreased CP content in sodium hydroxide treatment may be associated with increased ash content in this treatment, as the amount of ash is inversely related to the amount of OM. Hydrogen peroxide treatment significantly increased the ash content of cumin residues. We are not aware of any research on the effect of chemical processing on the mineral and ash content of cumin residue but, changes in mineral content have also been observed in other investigations that have used chemicals to treat fiber materials (Stehr 2019). Dehghani et al. (2021) found that urea processing increased ash in wheat straw and sugarcane bagasse. Treating rice straw and bagasse with sodium hydroxide and urea increased ash content in the Suksomabte study (Suksombat 2004). In the research of Moura et al., urea did not affect the ash level of dry acerola fruit residue, but it was higher in treatments with sodium hydroxide (Moura et al. 2020). The remaining sodium hydroxide may have influenced the higher ash levels. The ash content increased as a result of the use of sodium hydroxide to adjust the pH to 11.5 during hydrogen peroxide treatment. So, the increases in mineral and ash levels observed in cumin residue due to chemical treatments were expected because of the high mineral concentration of the chemicals utilized in this study. Alkaline-treated straws (such as sodium hydroxide and hydrogen peroxide) may be a better fiber source for ruminal buffering than untreated straws. This might help manage rumen acidity in animals fed high-grain diets and minimize the requirement for medicines to treat liver abscesses.

Cumin residue had lower levels of calcium, phosphorus, and salt than rice straw (Aquino et al. 2020). Calcium is required for strong bones and teeth, and salt aids in the maintenance of osmotic pressure, so treated cumin residue with hydrogen peroxide might help meet dietary requirements. The bioavailability of these minerals should be researched because most minerals are attached to other compounds in cumin residue in the form of acid-insoluble ash. Cumin residue's phosphorus level (160-225 mg/kgDM, or 0.022-0.016%) is insufficient to satisfy the needed 0.3 percent for animal growth and fertility.

Gas production parameters and digestibility

Table 3 shows the effects of chemical processing methods on cumin residue gas production parameters. All treatments reduced gas production potential and gas production rate significantly ($P< 0.01$). The most reduction in gas production potential and rate were obtained with sodium hydroxide and urea treatments, respectively. OMD, ME, and SCFA were significantly decreased by all chemical treatments (except for ME in sodium hydroxide treatment). Treatment with urea, hydrogen peroxide, and sodium hydroxide also decreased gas production compared to the control (Fig. 2).

Table 3 Effects of chemical processing methods on cumin straw gas production parameters

Treatments	a+b	c	OMD	ME	SCFA
Control	185.26^{a}	0.0101^{d}	44.85^{a}	3.20^{b}	0.743^{a}
Water	166.33^{b}	0.0922^{a}	41.15^{b}	2.21^{a}	0.650^{b}
Urea	164.73^{bc}	0.0659^{c}	38.34^{b}	2.21^{a}	0.583^{b}
H_2O_2	163.06^{d}	0.0791^{b}	38.48^{b}	2.21^{a}	0.586^{b}
NaOH	154.99^{c}	0.0745^{b}	38.71^{b}	3.20^{b}	0.590^{b}
SEM	0.863	0.0022	0.907	2.54	0.0228
P-Value	<0.0001	<0.0001	0.0021	0.0013	0.0022

$^{a,b.}$ Within the column, means with common superscripts do not differ ($P> 0.05$).
(a+b): Gas production potential (ml/gDM); c: Gas production rate (ml/h); OMD: Organic matter digestibility (% DM); ME: Metabolizable energy (MJ/kg); SCFA: Short chain fatty acids (mmol); SEM: Standard error of the mean.

DMD, OMD, partitioning factor (PF), and microbial mass production were all significantly affected by the chemical processing of cumin residues ($P< 0.05$; Table 4). Water treatment and sodium hydroxide had the greatest and lowest DMD, respectively. Compared to the control, hydrogen peroxide and sodium hydroxide treatments significantly reduced the OMD ($P< 0.01$). PF, microbial mass-produced after 24 hours of incubation (MCP), and microbial mass efficiency (EMCP) in water and urea treatments increased significantly compared to other treatments. The maximum gas production efficiency was obtained in the hydrogen peroxide and sodium hydroxide treatments (213.73 and 269.26 ml/gDM, respectively) and the lowest in the water treatment (173 ml/gDM). The pH and ammonia nitrogen levels were not affected by chemical processing methods.

Many by-products from the human food industry have high biomass, low CP level of 3 to 4%, and high crude fiber content of 35 to 48% in common. Cereal straws, sugarcane tops, bagasse, and other fibrous agricultural wastes are often fed to ruminants in many developing countries (Sarnklong et al. 2010). When other feeds are insufficient, fibrous agricultural byproducts are especially important. The digestibility of these compounds could be evaluated using the gas production technique. All chemical treatments reduced gas production, gas production potential (sodium hydroxide had a major influence), and increased gas production rate (Fig. 2 and Table 3) in this study. Gas production is directly related to substrate degradation (DM or OM degradation). The OMD, ME, and SCFA ranged from 38.31 to 44.85%, 2.21 to 3.20 MJ/KgDM, and 0.583 to 0.743 mmol, respectively, and all chemical treatments reduced SCFA compared to the control. We could not find any studies on cumin residue to compare the results with; however, it had less ME (5.32 to 11.12 MJ/KgDM) and SCFA (0.50 to 1.12 mmol) levels than maize chaff and rice straw (Mako and Rotimi 2020); However, cumin residue exhibited a similar OMD value to rice straw (37.53-44.58 percent) (Mako and Rotimi 2020).

Table 4 Effects of chemical processing methods on the digestibility and fermentation parameters of cumin straw

Treatment	DMD	OMD	PF	MCP	EMCP	Gas Yield	pH	$N\text{-}NH_3$
Control	52.26^{ab}	64.33^{ab}	3.83^{b}	103.87^{bc}	0.424^{b}	245.34^{ab}	6.82	0.83
Water	62.33^{a}	54.16^{a}	5.43^{a}	173.11^{a}	0.592^{a}	173.00^{d}	6.91	0.59
Urea	49.26^{b}	52.08^{bc}	5.11^{a}	134.22^{ab}	0.565^{a}	189.26^{cd}	6.90	0.69
H_2O_2	43.46^{bc}	42.97^{cd}	3.82^{b}	75.52^{cd}	0.422^{b}	213.73^{bc}	6.90	0.76
NaOH	35.20^{c}	33.78^{d}	3.19^{b}	47.35^{d}	0.306^{c}	269.26^{a}	6.87	0.79
SEM	3.39	3.47	0.256	13.44	0.03	11.71	0.09	0.04
P-Value	0.005	0.0011	0.005	0.0005	0.0003	0.001	0.001	0.456

$^{a,b.}$ Within the column, means with common superscripts do not differ (P> 0.05).
DMD: Dry matter digestibility (%); OMD: Organic matter digestibility (%); PF: Partitioning factor (mg OM truly degraded/ml gas produced in 24 h); MCP: Microbial crude protein (mg); EMCP: Efficiency of Microbial crude protein; Gas yield_{24}: The amount of gas production after 24 hours of incubation (ml); $N\text{-}NH_3$: Ammonia nitrogen (mg/dl); SEM: Standard error of the mean.

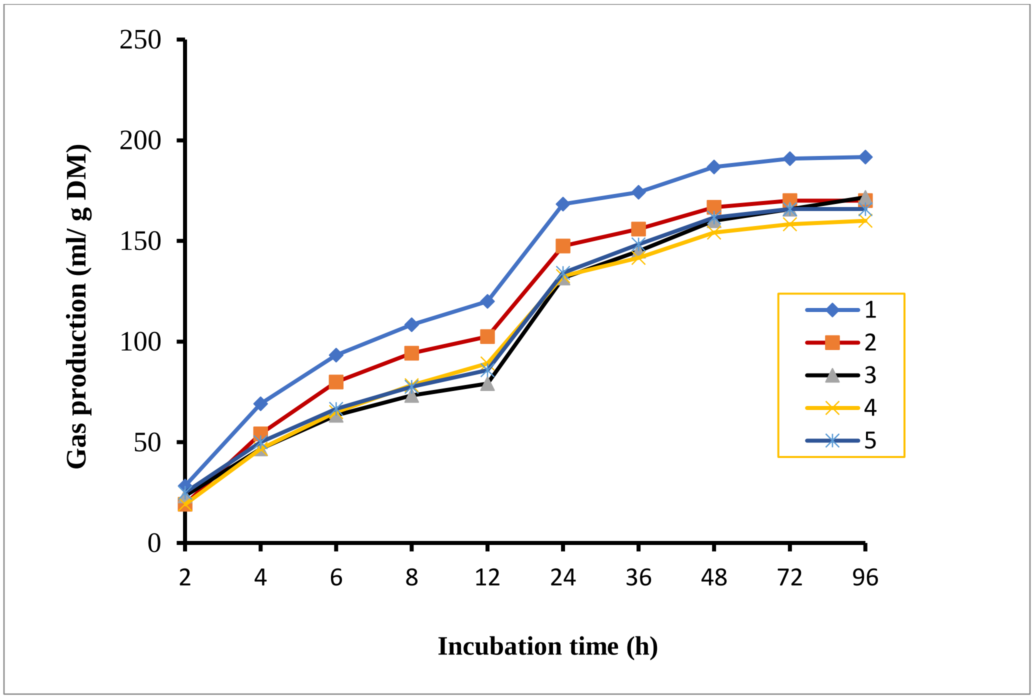

Fig. 2 Effect of chemical processing on cumin residue gas production

Treatment 1= Control (untreated cumin residue); Treatment 2= water treated cumin residue; Treatment 3= urea treated cumin residue; Treatment 4= hydrogen peroxide treated cumin residue; Treatment 5= sodium hydroxide treated cumin residue

In the sodium hydroxide treatment, cumin residues had the lowest DMD and OMD. Several studies were conducted *in vitro* (Liu et al. 2002; Suksombat 2004) or *in vivo* (Haddad et al. 1998; Ghiasvand et al. 2011; Mirzakhani et al. 2021) to treat various types of grain straws with chemical treatment with clear improvements in the nutritional and feeding value of treated straw. The in-situ degradability of bagasse and rice straw DM improved by treatments with 6% sodium hydroxide and urea (Suksombat 2004). It has been found that treating bagasse with 6% sodium hydroxide and rice straw with 6% urea is the most effective strategy for improving nutritional value and digestibility (Suksombat 2004). Suksombate, (2004) also reported a 22-unit increase in nylon bag DM degradability of bagasse treated with 6% sodium hydroxide. Sirohi and Rai (1995) revealed that a combination of 3% urea plus 4% lime at 50% moisture for three weeks was the most effective treatment for improving rice straw digestibility. *In vivo* studies have also shown that sodium hydroxide can improve the nutritional value, palatability, and intake of wheat straw (Haddad et al. 1994 and 1998). Calves-fed unprocessed wheat straw also had the lowest OM and DM digestibility compared to alkali-treated wheat straw (Mirzakhani et al. 2021). Processed straw has improved DMI in dairy cows (Mesfin and Ktaw 2010) and beef cattle (Ahmed et al. 2002). Unprocessed wheat straw exhibited lower fiber digestibility than processed wheat straw and needed more rumination to pass through the rumen (Mirzakhani et al. 2021).

The urea treatments did not affect the DMD and OMD levels of cumin residue. Conversely, urea treatment increased the DM and NDF potentially degradable fraction in wheat straw and sugarcane bagasse (Dehghani et al. 2021). The urea treatment also increased the DM and NDF degradability rate of wheat straw but did not affect sugarcane bagasse (Dehghani et al. 2021). The treatments of acerola fruit residue with urea (60 g/kgDM) and sodium hydroxide (40 and 60 g/kgDM) also provided the highest values of DM potential degradability (Moura et al. 2020). Zhang et al. (2018) observed that pretreatment of rice straw with urea (40 g/kgDM) decreased lignin concentration and improved *in vitro* rumen DM degradability. This is most likely due to the higher percentage of sodium hydroxide incorporation. Our study's chemical concentration seems to have been insufficient, so they had little effect on DMD and OMD. Moreover, the urea was degraded using the urease enzyme found in straw (Suksombat 2004), so the lack of urease enzymes in cumin residue or low urea levels may explain why urea treatments did not affect digestibility as compared to urea-treated in previous studies.

The PF value varied from 3.19 mg/ml (sodium hydroxide treatment) to 5.43 mg/ml (water treatment) in this investigation. In conventional diets, the PF has been found to range from 2.7 to 4.6 mg/ml (Blümmel et al. 1997a). A PF level over the normal range indicates the presence of an anti-nutritional component in the diet. The presence of anti-nutrient agents increases PF because these substances may be washed from the food during fermentation without making a role in the gas production process and disappearance of DM or preventing the solubility of other compounds, particularly proteins. In other words, nutrient dilution reduces microbial protein synthesis and gas production (McDonald et al. 1995). Poor digestibility of cumin residue is caused by several factors. The fiber is extremely resistant to degradation, partially due to the straw fiber's intrinsic qualities. The imbalanced nutrient availability, lack of easily available energy, low protein content, and low amount of essential minerals such as phosphorus and sulfur contribute to the degradation of straw fiber (Sarnklong et al. 2010). The sodium hydroxide works on the fibrous feeds by decreasing protein degradation and increasing delignification by breaking the connection between the cellulose and lignin components, allowing more time for microbial enzymatic activity (Aquino et al. 2020). No publications on the chemical treatment of cumin residue have been found, but the ratio of readily degradable CP fraction of rice straw improves, and the slowly degradable fraction decreased following urea treatments (Fadel Elseed et al. 2003). Straw, when combined with additional energy, protein, or minerals, improved rumen health and increases straw consumption. Rumen bacteria should be supplied with the nutrients they require for replication and growth to maximize the degradation of straw cell walls. This also provides the conditions for a sustainable cellulolysis process (Aquino et al. 2020).

Chemical processing did not affect pH of ammonia nitrogen levels. Similar to our findings, no differences in the mean or minimum rumen pH were detected as a result of barley straw CaO treatment in an *in vivo* research (Stehr 2019). Treated acerola fruit residue with urea and sodium hydroxide in concentrations of 20, 40, and 60 g/kgDM also did not affect pH (Moura et al. 2020). On the other hand, rumen pH increased when alkaline substances were added to the ration (Felix et al. 2012). Mirzakhani et al. (2021) found that ruminal pH decreased when a processed wheat straw diet was fed to the calves. Between 6.0 and 6.7 was shown to be the optimal pH for cellulose digestion, while pH below 6.0 prevented the development of bacterial species that contribute to fiber digestion. pH values below 5.5 reduced fibrolytics bacterial populations, indicating that fiber digestion may end entirely at these low pH levels (Mould et al. 1983).

In the urea treatment, increasing CP did not increase NH_3-N concentration (Table 4). In contrast to our findings, lambs given ammonia-treated wheat straw had higher ruminal NH_3-N concentrations 6 hours after feeding (Ribeiro et al. 2020). The 24-hour ammonia nitrogen level increased when urea was added to acerola fruit residue at concentrations of 40 and 60, but no effect had been seen when 20 g/kg DM was used (Moura et al. 2020). As previously stated, it appears that the urea concentration utilized in our investigation was insufficient for increasing ammonia nitrogen. Cumin residue has low bioavailability (poor digestibility and low protein concentration) compared to other forages thus it cannot provide the nutrients that high-yielding dairy cows require; however, it can be utilized as a fiber source in animals with lower nutritional needs.

Conclusion

Urea and hydrogen peroxide treatment could increase and decrease crude protein and fiber content of cumin residue, respectively. Aside from improving structural carbohydrate degradability, urea treatment can reduce the quantity of additional nitrogen required and lower the cost of acquiring protein-rich feedstuffs. However, the chemical concentration utilized in this experiment did not achieve the expected improvement in cumin residue digestibility. Given that no research has been performed so far to increase the quality of cumin residue and its usage for animal feed, it is suggested that future studies look at the effects of different treatment methods, such as biological and physical approaches, on improving the nutritional value of cumin residue.

Compliance with ethical standards

Conflict of interest The authors declare that there are no conflicts of interest associated with this study.

References

Ahmed S, Khan M, Shahjalal M, Islam K (2002) Effects of feeding urea and soybean meal-treated rice straw on digestibility of feed nutrients and growth performance of bull calves. Asian-australas. J Anim Sci 15:522-527. https://doi.org/10.5713/ajas.2002.522

Alaei A, Ghanbar F, Bayatkouhsar J, Farivar F (2019) Evaluation of nutritional value of vicia faba residues processed with some chemical compounds using in vitro and nylon bag techniques (In Persian). Anim Prod Sci 10:19-29. https://doi.org/10.29252/rap.10.26.19

AOAC (2005) Official methods of analysis. 18 Edition. Place Published: Publisher

Aquino D, Del Barrio A, Trach NX, Hai NT, Khang DN, Toan NT, Van Hung N (2020) Rice straw-based fodder for ruminants. In Sustainable Rice Straw Management pp. 111-129 .Springer, Cham

Bayat Kohsar J, Rezaii F, Mahmoudnia N, Ghanbari F (2021) The effect of fermentation by Bacillus subtilis and Aspergillus niger on the nutritional value of date palm kernels. J Anim Sci Technol9: 41-50. https://doi.org/10.22103/JLST.2021.17236.1359

Beauchemin KA, Ribeiro GO, Ran T, Milani MRM, Yang W, Khanaki H, Gruninger R, Tsang A, McAllister TA (2019) Recombinant fibrolytic feed enzymes and ammonia fibre expansion (AFEX) pretreatment of crop residues to improve fibre degradability in cattle. Anim Feed SciTechnol 256: 114260. https://doi.org/10.1016/j.anifeedsci.2019.114260

Blümmel M, Makkar H, Becker K (1997a) In vitro gas production: a technique revisited. J Anim Physiol AnimNutr 77: 24-34. https://doi.org/10.1111/j.1439-0396.1997.tb00734.x

Blümmel M, Steingaβ H, Becker K (1997b) The relationship between in vitro gas production, in vitro microbial biomass yield and 15 N incorporation and its implications for the prediction of voluntary feed intake of roughages. Br J Nutr 77: 911-921

Broderick G, Kang J (1980) Automated simultaneous determination of ammonia and total amino acids in ruminal fluid and in vitro media1. J Dairy Sci 63:64-75. https://doi.org/10.3168/jds.S0022-0302(80)82888-8

Chaudhry A (2000) Rumen degradation in sacco in sheep of wheat straw treated with calcium oxide, sodium hydroxide and sodium hydroxide plus hydrogen peroxide. Anim Feed Sci Technol 83: 313-323. https://doi.org/10.1016/S0377-8401(99)00134-0

Dehghani M, Afzalzadeh A, Norouzian MA (2021) The study of chemical composition and ruminal degradability parameters of urea treatment of wheat straw and sugarcane bagasse (In Persian). Anim Prod 23:191-200. https://doi.org/10.22059/jap.2021.316319.623583

Fadel Elseed A, Sekine J, Hishinuma M, Hamana K (2003) Effects of ammonia, urea plus calcium hydroxide and animal urine treatments on chemical composition and in sacco degradability of rice straw. Asian-australas. J Anim Sci 16: 368-373. https://doi.org/10.5713/ajas.2003.368

Felix T, Murphy T, Loerch S (2012) Effects of dietary inclusion and NaOH treatment of dried distillers grains with solubles on ruminal metabolism of feedlot cattle. J Anim Sci 90:4951-4961. https://doi.org/10.2527/jas.2011-4736

García-Martínez A, Albarrán-Portillo B, Castelán-Ortega OA, Espinoza-Ortega A, Arriaga-Jordán CM (2009) Urea treated maize straw for small-scale dairy systems in the highlands of Central Mexico. Trop Anim Health Prod 41:1487-1494. https://doi.org/10.1007/s11250-009-9337-4

Getachew G, DePeters E, Robinson P (2004) In vitro gas production provides an effective method for assessing ruminant feeds. Calif Agric 58:54-58. https://escholarship.org/uc/item/2078m8m1

Ghiasvand M, Rezayazdi K, Banadaki MD (2011) The effects of different processing methods on chemical composition and ruminal degradability of canola straw and its effect on fattening performance of male Holstein calves. J Anim Sci Res22: 93-104

Haddad S, Grant R, Klopfenstein T (1994) Digestibility of alkali-treated wheat straw measured in vitro or in vivo using Holstein heifers. J Anim Sci 72:3258-3265. https://doi.org/10.2527/1994.72123258x

Haddad S, Grant R, Kachman S (1998) Effect of wheat straw treated with alkali on ruminal function and lactational performance of dairy cows. J Dairy Sci 81:1956-1965. https://doi.org/10.3168/jds.S0022-0302(98)75769-8

Kahyani A, Ghorbani G, Alikhani M, Ghasemi E, Sadeghi-Sefidmazgi A, Beauchemin K, Nasrollahi S (2019) Performance of dairy cows fed diets with similar proportions of undigested neutral detergent fiber with wheat straw substituted for alfalfa hay, corn silage, or both. J Dairy Sci 102: 10903-10915. https://doi.org/10.3168/jds.2019-16869

Kulyar MF-e-A, Li R, Mehmood K, Waqas M, Li K, Li J (2021) Potential influence of Nagella sativa (Black cumin) in reinforcing immune system: A hope to decelerate the COVID-19 pandemic. Phytomedicine 85:153277. https://doi.org/10.1016/j.phymed.2020.153277

Liu J, Susenbeth A, Südekum K (2002) In vitro gas production measurements to evaluate interactions between untreated and chemically treated rice straws, grass hay, and mulberry leaves. J AnimSci 80:517-524. https://doi.org/10.2527/2002.802517x

Makar H (2004) Recent advances in the in vitro gas method for evaluation of nutritional quality of feed resources. FAO Animal Production and Health. Paper 55-88. https://www.fao.org/3/y5159e/y5159e05.htm

Mako AA, Rotimi OE (2020) Evaluation of nutrient content and in vitro gas fermentation of some crop residues as feed supplements for ruminants. ADAN J. Agric 1:123-130

Marcos CN, Carro MD, Yepes JF, Haro A, Romero-Huelva M, Molina-Alcaide E (2020) Effects of agroindustrial by-product supplementation on dairy goat milk characteristics, nutrient utilization, ruminal fermentation, and methane production. J Dairy Sci 103:1472-1483. https://doi.org/10.3168/jds.2019-17386

McDonald P, Edwards R, Greenhalgh J, Morgan C, Sinclair L, Wilkinson R (1995) Animal nutrition. Seventh Edition. Publisher: Prentice Hall. Hoboken, New Jersey. USA

Menke K, Raab L, Salewski A, Steingass H, Fritz D, Schneider W (1979) The estimation of the digestibility and metabolizable energy content of ruminant feedingstuffs from the gas production when they are incubated with rumen liquor in vitro. J Agric Sci 93:217-222. https://doi.org/10.1017/S0021859600086305

Menke KH (1988) Estimation of the energetic feed value obtained from chemical analysis and in vitro gas production using rumen fluid. Anim Res Dev 28:7-55

Mesfin R, Ktaw G (2010) Effect of feeding urea treated wheat straw based diet on biological performances and economic benefits of lactating Boran-Friesian crossbred dairy cows. Livest Res Rural Dev 22:12. http://www.lrrd.org/lrrd22/12/mesf22231.htm

Mirzakhani A, Ghorbani G, Sadeghi-Sefidmazgi A, Rafiee H, Drackley J (2021) Effects of starter protein content and alkali processing of wheat straw on growth, ruminal fermentation, and behavior in Holstein calves. J Dairy Sci 104: 3098-3108. https://doi.org/10.3168/jds.2020-19247

Mould F, Ørskov E, Mann S (1983) Associative effects of mixed feeds. I. Effects of type and level of supplementation and the influence of the rumen fluid pH on cellulolysis in vivo and dry matter digestion of various roughages. Anim Feed Sci Technol 10: 15-30. https://doi.org/10.1016/0377-8401(83)90003-2

Moura LML, da Silva Pereira FD, de Lima PR, Nascimento JCS, de Oliveira AdS, de Souza Rodrigues RT, Ferreira CP, Moraes SA, Queiroz MAÁ, Menezes DR (2020) Sodium hydroxide or urea pretreatment of acerola (Malpighia emarginata) fruit residue increases dry matter degradability and reduces methane production in in vitro rumen fermentation. Trop Anim Health Prod 52: 2433-2441. https://doi.org/10.1007/s11250-020-02272-z

NRC: National Research Council (2001) Nutrient requirements of dairy cattle. Seventh edition. Publisher: National Academy Press. Washington, D.C. USA

Ørskov E and McDonald I (1979) The estimation of protein degradability in the rumen from incubation measurements weighted according to rate of passage. J Agric Sci 92:499-503. https://doi.org/10.1017/S0021859600063048

Ramadan MF (2007) Nutritional value, functional properties and nutraceutical applications of black cumin (Nigella sativa L.): An overview. Int J Food Sci 42:1208-1218. https://doi.com/10.1111/j.1365-2621.2006.01417.x

Ribeiro GO, Gruninger RJ, Jones DR, Beauchemin KA, Yang WZ, Wang Y, Abbott DW, Tsang A, McAllister TA (2020) Effect of ammonia fiber expansion-treated wheat straw and a recombinant fibrolytic enzyme on rumen microbiota and fermentation parameters, total tract digestibility, and performance of lambs. J Anim Sci 98:skaa116. https://doi.org/10.1093/jas/skaa116

Sarkar C, Jamaddar S, Islam T, Mondal M, Islam MT, Mubarak MS (2021) Therapeutic perspectives of the black cumin component thymoquinone: A review. Food Funct. https://doi.org/10.1039/D1FO00401H

Sarnklong C, Cone J, Pellikaan W, Hendriks W (2010) Utilization of rice straw and different treatments to improve its feed value for ruminants: a review. Asian-australas. J Anim Sci 23:680-692. https://doi.org/10.5713/ajas.2010.80619

SAS (2003) SAS. In Book SAS, Vol., pp. (Ed.^Eds. Editor).Series SAS

Selim A, Pan J, Takano T, Suzuki T, Koike S, Kobayashi Y, Tanaka K (2004) Effect of ammonia treatment on physical strength of rice straw, distribution of straw particles and particle-associated bacteria in sheep rumen. Anim Feed Sci Technol 115:117-128. https://doi.org/10.1016/j.anifeedsci.2004.01.011

Sirohi S, Rai S (1995) Associative effect of lime plus urea treatment of paddy straw on chemical composition and in vitro digestibility. Indian J Anim Sci 65:1346-1351

Srinivasan K (2018) Cumin (*Cuminum cyminum*) and black cumin (*Nigella sativa*) seeds: Traditional uses, chemical constituents, and nutraceutical effects. Food Qual Saf 2:1-16. https://doi.org/10.1093/fqsafe/fyx031

Stehr KR (2019) Alkaline treatment of barley straw and its effect on digestibility, rumen fermentation. feedlot cattle performance and profitability. In Book Alkaline treatment of barley straw and its effect on digestibility, rumen fermentation. (Ed.^Eds. Editor). University of Saskatchewan

Suksombat W (2004) Comparison of different alkali treatment of bagasse and rice straw. Asian-australas J Anim Sci 17:1430-1433. http://sutir.sut.ac.th:8080/jspui/handle/123456789/882

Theodorou MK, Williams BA, Dhanoa MS, McAllan AB, France J (1994) A simple gas production method using a pressure transducer to determine the fermentation kinetics of ruminant feeds. Anim Feed Sci Technol 48:185-197. https://doi.org/10.1016/0377-8401(94)90171-6

Van Soest Pv, Robertson J, Lewis B (1991) Methods for dietary fiber, neutral detergent fiber, and nonstarch polysaccharides in relation to animal nutrition. J Dairy Sci 74:3583-3597. https://doi.org/10.3168/jds.S0022-0302(91)78551-2

Yimer EM, Tuem KB, Karim A, Ur-Rehman N, Anwar F (2019) Nigella sativa L.(black cumin): A promising natural remedy for a wide range of illnesses. Evid Based Complement Alternat Med 2019. https://doi.org/10.1155/2019/1528635

Zhang X, Wang M, Wang R, Ma Z, Long D, Mao H, Wen J, Bernard LA, Beauchemin KA, Tan Z (2018) Urea plus nitrate pretreatment of rice and wheat straws enhances degradation and reduces methane production in in vitro ruminal culture. J Sci Food Agric98:5205-5211. https://doi.org/10.1002/jsfa.9056