SILICA REMOVAL FROM RICE STRAW FOR ANIMAL FEED APPLICATION

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Dedicated to my beloved mak and ayah, abang and ammar

Thanks for your endless support and encouragement

Sorry for waiting so long...

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ABSTRACT

The large production of rice straw (731 ton/season) could eventually lead to uncontrolled air pollution due to open burning activity. Although rice straw has been used as animal feed since in the 1980s, it has failed to provide sufficient amount of protein for daily ruminant growth (about 15-20%). Hence, this study explored the use of rice straw waste for animal feed that can provide the amount of protein needed for daily ruminant growth. Moreover, as silica has been discovered as the main hurdle in animal feed processing, the rice straw sample was treated with alkaline hydrogen peroxide (AHP) via batch and continuous systems. Besides reducing the silica content, it is also aimed to maximize the protein content of the treated rice straw. Meanwhile, in the continuous system, a single column packed bed with up-flow system was adapted before carrying out further biological treatment with the fungi, Neurospora sitophila for cell protein production. Other than that, physical and chemical characterizations of rice straw sample (obtained from Seberang Perak, Malaysia) were conducted before and after pretreatment processes to determine the effectiveness after each pretreatment process. From the results obtained, a kinetic study was carried out to investigate the removal behavior for each system. From the characterization analysis, the rice straw sample was found to contain a high level of silica (20%) and lignin (20%), but very low-level protein content (6-7%). Besides, the batch process of pretreatment with AHP, as well as the effects of different parameters (i.e. AHP concentrations, particle sizes of rice straw, and temperature) had been studied. From the batch process, the optimum condition obtained was at 60°C with application of 10% of AHP solution for sample with < 0.5mm particle size. At this condition, more than 83.8% of silica removal, 80% of delignification, and 7.88% of reduced sugar production were achieved. On the other hand, as for the continuous AHP pretreatment process, and followed by biotreatment of Neurospora sitophila (edible fungus) in the single column, it was found that 84% of silica was removed with 80% of delignification and 8% of reduced sugar production with 10% AHP solution in a 7cm treated and compacted rice straw bed at room temperature. Furthermore, the protein content in the pretreated rice straw increased by a whopping 80%. Meanwhile, the kinetic study revealed that both the batch and the continuous silica removal processes were highly influenced by mass transfer, in comparison to the other steps. Hence, it can be concluded that this study has depicted that the selected processes for silica removal and protein enhancement of local rice straw are indeed suitable for animal feed production. Additionally, the kinetic study has been proven beneficial in understanding the attributes of the removal process.

ABSTRAK

Penghasilan jerami padi berskala besar (731 tan/ musim) menyumbang kepada pencemaran udara yang tidak terkawal yang terhasil dari pembakaran secara terbuka. Jerami padi juga gagal untuk menyediakan jumlah protein yang mencukupi untuk tumbesaran harian ruminan walaupun ianya telah mula digunakan dalam penghasilan makanan ternakan semenjak tahun 1980 (15-20%). Oleh itu, kajian ini meneroka penggunaan jerami padi dalam penyediaan makanan ternakan yang boleh menampung keperluan protein dalam tumbesaran harian ruminan. Disebabkan silika adalah penghalang utama dalam proses penyediaan makanan ternakan, perawatan jerami padi menggunakan hidrogen peroksida beralkali dalam bentuk kelompok dan berterusan dijalankan. Tujuan utama kajian ini adalah untuk menambahbaik kandungan protein selain mengurangkan kandungan silika dalam jerami padi. Dalam sistem berterusan, silinder mampatan di mana aliran hidrogen peroksida beralkali dari bawah ke atas digunakan untuk rawatan pembuangan silika daripada jerami padi sebelum rawatan biologi menggunakan kulat, Neurospora sitophila di dalam silinder yang sama. Dalam kajian ini penentuan karakter jerami padi secara fizikal dan kimia yang diambil dari Seberang Perak, Malaysia dilakukan sebagai penanda aras keberkesanan rawatan yang digunakan. Dari dapatan kajian ini, kajian kinetik yang ringkas telah dilaksanakan untuk menerangkan tabiat pemisahan silika dari jerami padi yang berlaku dalam setiap sistem. Daripada analisis, sampel jerami padi didapati mengandungi tahap silika (20%) dan lignin (20%) yang tinggi beserta kandungan protein yang sangat rendah (6-7%). Proses rawatan dalam sistem kelompok yang menggunakan hidrogen peroksida beralkali, di mana faktor berbeza yang menyumbang kepada proses pemisahan (kepekatan bahan perawat, saiz jerami dan suhu) dikaji. Daripada proses kelompok, tahap pemisahan yang optimum didapati pada suhu 60°C dengan penggunaan 10 % kepekatan hidrogen peroksida beralkali pada sampel dengan saiz jerami < 0.5mm. Pada keadaan ini, lebih 83.8% silika telah berjaya dipisahkan dari jerami, 80% nilai pengurangan lignin dan 7.88% gula ringkas juga dapat dihasilkan. Dalam sistem berterusan pula 84% nilai silika dapat dipisahkan dan 80% nilai lignin juga dapat dikurangkan dan 8% jumlah gula ringkas dapat dihasilkan dengan 10% agen pemisah dan 7cm mampatan jerami padi terawat pada suhu bilik. Nilai protein di dalam jerami padi terawat bertambah sebanyak 80%. Daripada kajian kinetik, ianya juga didapati bahawa sistem pemisahan silika secara kelompok dan berterusan amat bergantung pada faktor pemindahan jisim berbanding faktor lain. Kajian ini dapat disimpulkan di mana proses yang dipilih amat sesuai untuk pemisahan silika dan penambahbaikkan nilai protein jerami padi tempatan untuk menghasilan makanan ternakan khususnya. Kajian kinetik yang dijalankan juga sangat bermanfaat untuk pemahaman tabiat dalam proses pemisahan silika dari jerami padi.

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LIST OF ABBREVATIONS

A - Cross-sectional area

AHP - Alkaline Hydrogen Peroxide

C_A - Concentration of dissolved solid in the bulk of

solution

C_{ad} - Concentration of silica adsorbed to AHP agent at

certain flow time

CAP - Catabolite Activator Protein

CP - Crude Protein

DM - Dry Matter

DSMZ - Deutsche Sammlung von Mikroorganismen und

Zellkulturen

EM - Effective Microorganisms

Fe(NO)₃ - Iron Nitrate

FELCRA - Federal Land Consolidation and Rehablitation

Authority

FESEM - Field Emission Electron Microscopy

FIBEX - Fiber Extrusion Technology

FTIR - Fourier Transform Infra Red

L. - Lactobacillus.

LAB - Lactic Acid Bacteria

 M_{total} - Total mass of silica adsorbed by the AHP agent

MARDI - Malaysian Agricultural Research and Development

Institute

MBTH - 3-methyl-2-benzothiazolinone hydrazone

hydrochloride

MTZ - Mass Transfer Zone

N - Normality

N₀ - Saturation concentration

NDF - Neutral Detergent Fiber

OD - Optical Density

OPF - Oil Palm Fiber

PAH - Polycyclic Aromatic Hydrocarbon

PELADANG - Lembaga Pertubuhan Peladang Malaysia

SCP Single cell protein

SSF - Solid state fermentation

YEFECAP - Yeast Fermented Cassava Chop Protein

 μ - Solvent viscosity

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CHAPTER 1

INTRODUCTION

1.1 Background of the Study

The Food and Agricultural Organization Rice Market Monitor (FAO RMM) claimed that the global paddy production for the 2015 season was 738 million tons and this number was predicted to hike up to 750 million tons by end of 2016 (FAO, 2016). Furthermore, the Malaysian FAO had also estimated that the national output had grown by four percent to 2.6 tons (1.7 million tons on milled basis). In fact, Kedah has possessed the highest area of paddy plantation, which is 200 thousand hectares of cultivation area, as presented by the Malaysian Agriculture Department in Figure 1.1. In general, these agricultural wastes are burnt if non-recyclable or non-reusable. Such burning deteriorates the quality of air and causes air pollution; thus posing threat to people's health, as the minute PAH can easily penetrate into one's pulmonary alveoli (Yang *et al.*, 2005).

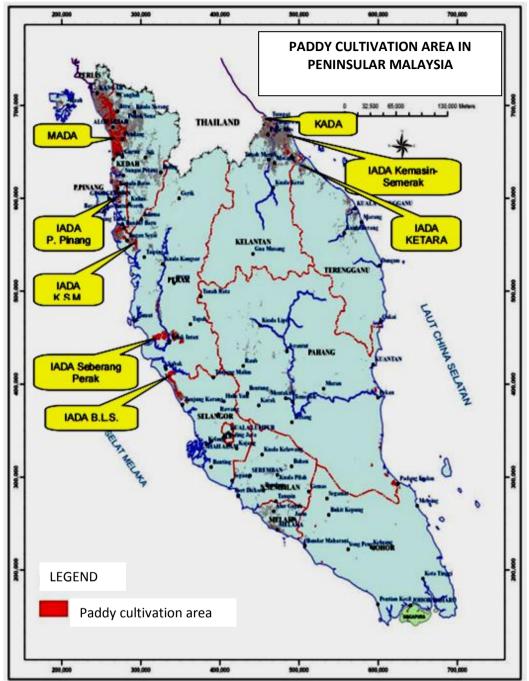


Figure 1.1 Map of paddy area in Malaysia 2013 (Soil Management Division, Department of Agriculture, Peninsular; MADA: Muda Agricultural Develoment Authority; IADA: Intra-Asia Discussion Agreement; KADA: Kemubu Agricultural Develoment Authority)

Therefore, instead of burning, rice straw can be potentially applied for silage production. However, it is a challenge to use rice straw as a silage due to the low protein content in rice straws that poses as a barrier to be directly fed to animal, especially for ruminant. This is because; a minimum requirement of nutrient content has been determined by the Malaysian Department of Veterinary. Basically, ruminant needs more than 15% of protein content for growth, as well as to produce standard quality of milk and meat. The crude protein content of rice straw is way below than the requirement, as reported in rice straw source from other countries, such as at 5.4% and 5.8% in India and China (Jian-Xin *et al.*, 2001), 4.6% in California (Nader & Robinson, 2008), 5.7% in Japan (Fang *et al.*, 2012), and 5.65% and 2.5% in Ghana and Thailand respectively (Wanapat *et al.*, 2009). Thus, vast protein improvements are required (above 100% from original values) to achieve the target (Van-Soest, 2006).

Protein is the most crucial nutrient for weight gain and gestation. From prior investigations, a combination of treatments can efficiently improve the performance of rice straw as an animal feed. For instance, the combination of chemical and supplementation (52.92% rice straw + 30% cassava + 15% cotton seed meal + 2.08% urea) offers 12% of crude protein (Sommart et al., 1999), which is similar to chemical and biological combination, as conducted by Van-Soest (2006), Chen et al., (2008), Su et al., (2012), and Fang et al., (2012). Besides, the combination of chemical and supplementation (100 g rice straw + 100 g ammonia bicarbonate + 300 ml water + 5% Chinese milk vetch silage) gives 20.2% of crude protein (Liu et al., 1997), (rice straw + ammonia bicarbonate + rapeseed meal + water) provides 21% of crude protein (Liu et al., 2001), (1 kg rice straw + 500 ml water + 45 g urea + 10 ml of 20% sulphuric acid + concentrates that consist of rice bran + ground corn + avoparcin) results in 17.1% of protein content (Soodeen-Karamath & Youssef, 1999). Other than that, the physical and chemical combination (Shen et al., 1998; Ware & Zinn, 2005), as well as the combination of physical, chemical, and supplementation (40% of chopped rice straw + 60% of concentrates that consist of corn + soy bean meal + rapeseed meal + urea + premix), gives 13.8% protein content (Wang et al., 2011). Lastly, Fiber Explosion (FIBEX), which consists of treatment via steam with ammonia concentrates, also offers 18% of rice straw (Weimer et al.,

2003). Nonetheless, such combination methods lead to higher costs for the production of animal feed.

Therefore, probe into new alternatives and unconventional protein sources has taken place to fulfill the needs of protein for ruminant. For instance, in 1996, a new protein source was discovered, termed as 'single cell protein' (SCP) or microbial protein development, mainly deriving from yeast, bacteria, and fungi to enhance the protein level in biomass (Rasoul-Amire *et al.*, 2011). This microbial protein production can be considered as an effective alternative, especially for the production of animal feed from agricultural wastes. In fact, early studies showed that cellulose from agricultural waste possesses high potential as substrates from SCP application (Martin, 1991; Bekatorou *et al.*, 2006; Nasseri *et al.*, 2011).

Similarly, rice straw also contains high amount of complex structure that is comprised of hemicelluloses, cellulose, lignin, and silica, hence making the aspect of digestibility rather low due to the large degree of ester bonding in hemicelluloses (Van-Soest, 2006). Thus, in order to remove this carbohydrate, lignin, and silica complex structure, several types of pretreatment methods, such as alkali, steam explosion, grinding, ammonia fiber via substitutions to silicic acid and silicon dioxide, could be carried out (Nader & Robinson, 2008).

The silica substance may become a major contributing factor to the resistance for the degradation of rice straw, which is hindered by the process of maximizing sugar reduction (Bae *et al.*, 1997; Agbagla-Dohnani *et al.*, 2003). This factor, unfortunately, has been neglected in numerous treatment studies. During the degradation process, hemicelluloses and lignin are normally removed. The high content of biogenic silica in the wall of epidermal cell layer, which results from the application of fertilizers, irrigation, and harvest time, could influence the degradation process of rice straw (Shen *et al.*, 1998). Moreover, treatments for silica removal are indeed required due to the larger amount of silica content in rice straw, which cannot be simply dismissed. Furthermore, Sun *et al.*, (2000) discovered that rice straw contains average silica content that ranges from 0.05 to 20.00%.

In addition, some studies detected that the highest level of silica is found in rice straw, followed by wheat straw, sorghum, rye, maize, and barley (Tamai & Jian, 2003). The silica is converted to silicic acid and later, transported to the plant structures. Besides, the silica concentration is higher in older tissue leaves compared to stem (Mecfel *et al.*, 2007). In fact, one should note that silica (group 14 in the periodic table) is not an essential mineral for a plant, but it offers several benefits, such as increased resistance to chemical and physical stresses, added strength and stiffness, as well as increased pest resistance.

Silica, which is typically known as silicon dioxide, is probably the first limiting factor in straw rice quality because silica has diverse metabolic functions and it is involved in carbohydrate synthesis that generates a negative association with digestibility (Van Soest, 2006). Normally, the level of silica in rice straw is about 8.3% (Gu et al., 2013) and 9-10% (Bae et al., 1997), depending on the plant location and other factors. Based on several other sources, 20% of silica content in rice straw makes it an attractive source for amorphous silica production. The amount of silica present in the various components of the rice plant consists of 0.5g/kg of polished rice, 50g/kg for rice bran, 130g/kg for rice straw, 230g/kg for rice hulls, and 350g/kg for rice joints (Van Soest, 2006). Hence, silica can be applied in solar cells, drug delivery, and for application in the biomedical field (Rehman et al., 2013). Nevertheless, silica impedes soda and craft processes related to paper production. Compared to other crops, the variances of silica content depend on the photosynthetic mechanisms of the grass and the amount of water transferred to the grass. For example, cereal straw contains high silica level, where wheat straw possesses 4-10% of silica, while rice straw has a higher value of silica, which is 9-14%, and other cereals like barley, oat, and rye straws possess 1-6% of silica level (Pekarovic, 2005).

Additionally, silica can exist in amorphous (glass) and a variety of crystalline (quartz, tridymite, and cristobalite) forms. Normally, it is deposited as amorphous silica, which is mainly located in the epidermal cell. On top of that, silica normally covers the outer surface of the plant stem and morphologically, silica is the thickest

outer layer of plant bodies, especially in rice straw. Meanwhile, in living plants, silica is present in three basic forms: insoluble silica, colloidal silicic acid, and silicate ions, but almost 90% of it is present as insoluble silica. In other sources, the epidermal surface of rice straw contains high concentration of silica and it is covered by cutin and waxy layers. Furthermore, silica is extremely soluble in alkaline condition and must be removed from recovery cycle, especially in the pulping process to avoid mechanical error during the process.

In fact, other studies also showed that the digestibility of roughages could be increased via alkali treatment, where partial solubilization of hemicellulose, lignin, and silica occurs first (Bae *et al.*, 1997). Besides, silica always functions as the physical barrier, which prevents bacterial attachment and causes inefficient digestion of plant cell wall carbohydrates.

On the other hand, the desilication process refers to the elimination of silica, which normally occurs in craft pulping industry plant. Numerous techniques for desilication are available, such as black liquor desilication with carbon dioxide (flue gasses), two-stage causticizing method, green liquor desilication with lime, and the use of sodium carbonate as a silica-leaching agent, which can lead to 50-75% of desilication rate (Pekarovic *et al.*, 2005). Furthermore, silica also gives small dissolution effect in pure water, especially in the presence of other species like sodium chloride or when higher temperature is applied (Xiao *et al.*, 2010). In comparison to the use of pure water, the rate of silica dissolution is higher by 18-30 times with the presence of other organic electrolyte. In fact, the parameters that have been investigated to attain optimum desilication process are temperature, time, and chemical charge. As a result, temperature and time portrayed the strongest influence, but unfortunately, removed several organic compounds in that process.

The previous section depicts some evidences pertaining to silica that could be dissolved with strong alkaline. This process is known as 'depolymerisation', and further catalysis with hydroxyl ion could result in a five-coordinate center by weakening the other oxygen bonds. The rate of this reaction depends on the ability

of hydroxyl ion, the silica structure, and the pH of the solution. Besides, prior studies have shown that the removal increases in line with the alkalinity level of the solution (Iler, 1979). Other than density of materials; surface area, temperature, and pressure also can affect the rate of silica removal (Zotov & Kepler, 2002).

Nonetheless, the use of strong alkaline alone is inadequate to cater the amount of hydroxyl ions needed for high silica removal. In fact, hydrogen peroxide functions as both the proton donor and the proton acceptor (Zeglinski *et al.*, 2006). These hydrogen peroxide molecules establish the ability to form stronger bonds with silicon than water molecules do if they function as proton acceptor. This further generates hydroxide radicals that enhance the removal rates. Hence, the discussion above portrays that hydroxyl ions may react with silica in rice straw and form silicic acid, Si(OH)₄. The mechanisms show that Si-O- sites react with –OH sites to form silicic acid in abundant (Manivannan & Ramanathan, 2009). Later, the high amount of silicic acid leads to higher formation of silicate ion via condensation process by incorporating hydroxyl ion. Thus, the presence of silicate ions increases the solubility of silica, thus completing the removal process.

1.2 Problem Statement

In addition, the statistics shows abundance of rice straw due to the increasing production annually, making it the most waste that needs to be recycled into other products with high value like silages (animal feed products). However, it is important to acknowledge that conventional silage fermentation (anaerobic fermentation) has failed to at least maintain the protein level in rice straw without any supplementation for animal feed (concentrated) application. Moreover, it takes at least months to complete the fermentation process.

The high quality of silage must retain the original level of protein with high nutrient level that has the ability to stabilize the essential characteristics without being contaminated with fungus or mold. Silage is normally served with supplements called concentrations (combination of high nutrient supplements) that enrich the protein content, thus increasing the cost of feed. In part of that, using urea as additives can increase the protein content in rice straw, but it has adverse effects Therefore, microorganisms ruminants. like bacteria and microorganisms (EM) have been employed as alternatives. The results of microbiology application, in fact, have indicated that the best approach is applying edible fungus that can secrete enzyme by utilizing carbon from lignicellulosic material, such as rice straw, through the progress of SCP.

Nevertheless, the high silica content (from the very complex structure) of rice straw must be removed first through a pretreatment method because it becomes a distraction for carbon source production to be consumed by fungus, along with the secretion process. Normally, rice straw protein improvement should begin with the delignification process. The lignin is removed to enhance the enzymatic attack on the rice straw structure. Past researchers, unfortunately, failed to highlight the issues concerning silica upon rice straw structure. In the first place, silica (SiO₂) has an important role in plant yield, especially rice (Sahebi et al., 2015), for it is a beneficial nutrient supply through fertilizer. Some studies also depicted that the grain yield of plants with silica is double than plants without silica. Physiologically, the silica layer has the ability to increase the resistance towards fungi, bacteria, and insect pest attack (as illustrated in Figure 1.2). The silica is still located at the same place even after the plant becomes a waste (after harvest) and even increases by storage time (increased directly with maturation time). However, after becoming waste, the silica becomes non-beneficial due to its application as an inert substrate. Therefore, during post-application, especially when fungi/yeast/bacteria grow on the straw surface without any resistance, the process of silica removal must be carried out as a preparation. Silica removal pretreatment must first be performed before other posttreatment is conducted on inert substrate like animal feed and biofuel production.

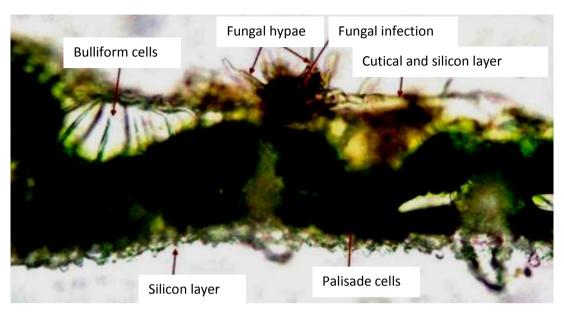


Figure 1.2 Role of silica deposition in bamboo leaf during fungal attack (Mahbod *et al.*, 2015)

Leaching is the process of extracting a soluble constituent from a solid using a solvent. Therefore, this process is suitable to represent the silica removal method from rice straw with alkaline hydrogen peroxide (AHP) as a solvent. This is a technique used either to extract a valuable constituent from the solid or to remove a solid from a soluble material. Hence, in order to clarify the mechanisms of silica removal during this process of pretreatment, it is important to perform a kinetic study before focusing on the edible fungus application in order to determine if the rate of removal process is highly influenced by diffusion or chemical reaction. Hence, the results can be highly valuable for scaling up or for further optimization study.

Moreover, batch system data are more suitable for small-scale treatment volumes, but inconvenient for large-scale application due to several factors. Therefore, in order to get more realistic laboratory results, the packed bed column study is essential since it has greater resemblance to the flow condition in the later full-scale application. Moreover, it is also significant to predict the behavior of column breakthrough curve, which can offer a functional life span of the column bed. Summing it up, the fundamental mechanisms of silica dissolution process from rice straw must deeply focus on the batch system to attain the main objective, which is to

remove silica, as well as to enrich the protein content of rice straw via microbial protein production technology in continuous system.

1.3 Objectives

As a whole, this study is aimed to maximize the required protein content in rice straw-based silage through the combination of Alkaline Hydrogen Peroxide (AHP) and edible fungus (*Neurospora sitophila*) treatments. As such, the following are the objectives of this research work.

- 1) To investigate the effects of the various hydrogen peroxide (H₂O₂) concentrations in alkaline condition, particle sizes, and temperature in batch AHP process towards silica removal, delignification, and sugar reduction production in pretreated rice straw
- 2) To investigate the AHP pretreatment in continuous system, as well as to investigate the effects of various hydrogen peroxide (H_2O_2) concentrations and the length of rice straw bed in alkaline condition towards the percentage of silica removal, delignification, and sugar reduction production.
- 3) To study the kinetic mechanisms of silica removal from rice straw via alkaline hydrogen peroxide (AHP) pretreatment (batch and continuous) to enhance the production of reduced sugar.
- 4) To investigate the effectiveness of microbial cell protein production in pretreated rice straw by edible fungus application called *Neurospora Sitophila*

1.4 Scope of Study

From each objective, the scope of study is listed in the following:

- 1) To study the kinetics effect of the various hydrogen peroxide (H₂O₂) concentrations in alkaline condition (0-10%), particle sizes (less than 0.5 mm, 0.5-1.0 mm, and more than 1.0 mm), and temperature (30-60 °C) on the percentage of silica removed at a fixed solid and liquid ratio, shaking speed, and volume in the batch system.
- 2) To study the kinetics effect of various hydrogen peroxide (H₂O₂) concentrations (0-10%) and length of rice straw bed in alkaline condition (7cm and 12cm) on the percentage of silica removal at fixed feeding rate, particle size, temperature (limitation of the equipment), and volume in continuous system (fixed bed column).
- To study the behavior of kinetic mechanism for silica removal from rice straw through the application of diffussion/chemical reaction shrinking core models in batch process and STATISTICA software program, as well as the nature of equilibrium for silica removal from rice straw via breakthrough curve analysis using Thomas and Adams-Bohart models.
- 4) To study the biomass and the morphological aspects on adhesion effect of fungus on the solid surface of rice straw, as well as protein enrichment application study for various conditions of pretreated rice straw at a fixed weight when *Neurospora sitophila* was applied.

1.5 Significances and Original Contributions of This Study

The significances of this study can be divided into a three aspects: the effectiveness of silica removal, the kinetic behavior of that process, and the protein enrichment of treated rice straw sample. The original contribution of knowledge would be in terms of the high association between silica removal and reducing sugar enrichment trend, which are profoundly significant in this study. This is because; prior studies only focused on reducing sugar enrichment for further application without considering the kinetic behavior of the treatment process. This knowledge is not only for animal feeds application, but it is also essential for the production of alcohol and biofuel from various types of agricultural wastes. Furthermore, as the AHP pretreatment for reducing sugar and the usage of Neurospora Sitophila for protein enrichment had been separately proven previously by prior researchers, the kinetic study, especially the value of the kinetic coefficient for silica removal, is important for research and development in the agricultural industry like scaling up and optimization study. Besides, the usage of this continuous system for both processes that occur in the same vessel is also essential for other applications. For instance, acceleration of alcohol products from corn waste by using strains of bacteria or fungus.

Second, this study contributes to the research development in Malaysia. Research pertaining to agricultural study, especially for animal feeds application that focuses on knowledge enhancement and economic developments, is still limited. The continuous system developed in this study, hence, can be expanded into a pilot plant study, whereas factory scale for business purposes. Finally, this study is also beneficial for various levels of farmers in the stance of economic development, including conventional farmers and government or private sectors (MARDI, FELCRA, and PELADANG). Furthermore, the application of *Neurospora Sitophila* for nutrient enhancement of animal feeds has been widely applied in various nations, thus it can be identified as a functional and reliable technology for Malaysian farmers in near future.

REFERENCES

- Abasiekong, S. F. (1991). Effect of fermentation on crude protein and fat contents of crushed grains of maize and sorghum. *Journal of Application Bacteriol*. 70: 391-393.
- Abdel Aal E. A. (2000). Kinetics of sulfuric acid leaching of lowgrade zinc silicate ore. *Hydrometallurgy*. 55: 247–254.
- Abu-Tarboush, H. M., & Ahmed, S. A. B. (1996). Studies on karkade (Hibiscus sabdariffa): protease inhibitors, phytate, in vitro protein digestibility and gossypol content. *Food chemistry*, *56*(1), 15-19.
- Adjorlolo, L., Amarning-kwating, K., and Fianu, F. (2001). In vivo digestibility and effect of supplemental mucuna forage on treated rice straw degradation. *Small Ruminant Research*. 239-245.
- Agbagla-Dohnani, A., Noziere, P., Gaillard-Martinie, B., Puard, N. and Doreau, M. (2003). Effect of silica content on rice straw ruminal degradation. *Journal of Animal Science*. 140:183-192.
- Ahamed, A. and Vermette, P. (2008). Culture-based strategies to enhance cellulase enzyme production from *Trichoderma reesei RUT-C30* in bioreactor culture conditions. *Biochemical Engineering Journal*. 40(3):399-407.
- Ahmad, A.A. and Hameed, B.H. (2010). Fixed-bed adsorption of reactive azo dye onto granular activated carbon prepared from waste. *Journal of Hazard Materials*. 175 (1–3): 298–303.
- Akin, D.E., Rigsby, L.L., Sethuraman, A., Morrison, W.H.-I.I.I., Gamble, G.R. and Eriksson, K.E.L. (1995). Alterations in structure, chemistry, and biodegradability of grass lignocellulose treated with the white rot fungi *Ceriporiopsis subvermispora* and *Cyathus stercoreus*. *Applied Environmental Microbiology*. 61:1591–1598.

- Aksu, Z. and Gonen, F. (2004). Biosorption of phenol by immobilized activated sludge in a continuous packed bed: prediction of breakthrough curves. *Process Biochemistry* . 39 (5): 599–613.
- Albores, S., Pianzzola, M.J., Soubes, M. and Cerdeiras, M.P. (2006). Biodegradation of agroindustrial wastes by *Pleurotus spp* for its use as ruminant feed. Electron. *Journal of Biotechnology*. 9:215–220.
- Al-Muhtaseb, S.A. and El-Naas, M. (2008). Removal of aluminium from aqueous solutions by adsorption on BDH activated carbons. *Journal of Hazardous Materials*. 1(58):300-307.
- Alvarez-Vasco, C. and Zhang, X. (2013). Alkaline hydrogen peroxide pretreatment of softwood: Hemicellulose degradation pathways. *Bioresource Technolog*. *150*: 321-327.
- American Society for Testing and Materials. *Annual Book of American Society for Testing and Materials Standards*, *Part 6*; *Part 21*; *Parts 27-28*, University of California, April 1983.
- Araujo, L. D., Medeiros, A. N., Neto, A. P., Oliveira, L. D. and da Silva, F. L. H. (2005). Protein enrichment of cactus pear (Opuntia ficus-indica Mill) using Saccharomyces cerevisiae in solid-state fermentation. *Brazilian Archives of Biology and Technology*. 48: 161-168.
- Aris, R. (1975) The Mathematical Theory of Diffusion and Reaction in Permeable Catalysts; Clarendon: Oxford.
- Arora, D.S. and Sharma, R.K. (2009). Enhancement in in vitro digestibility of wheat straw obtained from different geographical regions during solid state fermentation by white rot fungi. *Biological Resources*. 4:909–920.
- Arvanitoyannis, I. and Tserkezou, P. (2006). Corn and rice waste: a comparative and critical presentation of methods and current and potential uses of treated waste. *International Journal of Food Science and Technology*. 958–988.
- Ashour, S.A., Elsharabasy, M.M.H. and Khalil, A.M. (1993). Conversion of rice straw to high protein animal feed by discontinuous gradient fed-batch fermentation. *Journal of University Kuwait Science*. 20:275–282.
- Aydogan, S., Aras, A. and Canbazoglu, M. (2005). Dissolution kinetics of sphalerite in acidic ferric chloride leaching. *Chemical Engineering Journal*, 114(1–3): 67-72.

- Azzam, M. (1989). Pretreatment of cane baggase with alkaline hydrogen peroxide for enzymatic hydrolysis of cellulose and ethanol fermentation. *Journal of Environmental Science Health*. 24(4): 421-433.
- Bae, H. D., McAllister, T. A., Kokko, E. G., Leggett, F. L., Yanke, L. J., Jakober, K.
 D. and Cheng, K. J. (1997). Effect of silica on the colonization of rice straw
 by ruminal bacteria. *Animal Feed Science and Technology*.65(1–4):165-181.
- Bai, S., Mu, H., Naren, G., Okaue, Y. and Yokoyama, T. (2014). Kinetic study of silica dissolution in aqueous solutions of aromatic organic electrolytes. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 461:220-224.
- Ballesteros, I., Oliva, J.M., Navarro, A.A., Gonzalez, A., Carrasco, J. And Ballesteros, M. (2000). Effect of chip size on steam explosion pretreatment of softwood. *Appllication Biochemical Biotechnology*. 84(6):97–110.
- Banerjee, U. C., Chisti, Y. and Moo-Young, M. (1995). Effects of substrate particle size and alkaline pretreatment on protein enrichment by *Neurospora sitophila*. *Resources, Conservation and Recycling*, *13*(2): 139-146.
- Banerjee, G., Car, S., Scott-Craig, J.S., Hodge, D.B. and Walton, J.D.(2011.) Alkaline peroxide pretreatment of corn stover: Effects of biomass, peroxide, and enzyme loading and composition on yields of glucose and xylose. *Biotechnology Biofuels* 4:16.
- Banerjee, K., Ramesh, S.T., Gandhimathi, R., Nidheesh, P.V. and Bharathi, K.S. (2012). A novel agricultural waste adsorbent, watermelon shell for the removal of copper from aqueous solutions. *Journal of Environmental Health Science Engineering*. 3 (2), 143–156.
- Balat, M., Balat, M., Kirtay, E. and Balat, H. (2009). Main routes for the thermo conversion of biomass into fuels and chemicals.Part 1:pyrolysis system. *Energy Conversion Management*.50:47-57.
- Balat, M. (2011). Production of bioethanol from lignocellulosic materials via the biochemical pathway: A review. *Energy Conversion and Management*, 52(2): 858-875.
- Bass, A.E., D. Philipp, K.P. Coffey, J.D. Caldwell, R.T. Rhein, A.N. Young, W.K. Coblentz. (2012). Chemical composition, intake by sheep, and in-situ disappearance in cannulated cows of bermudagrass hayed at two moisture

- concentrations and treated with a non-viable Lactobacillus actic acid preservative. *Animal Feed Science and Technology* 117:43-51.
- Bekatorou, A., Psarianos, C. and Koutinas, A.A. (2006). Production of food grade yeasts. *Food Technology and Biotechnology*., 44: 407 415.
- Ben Sik Ali, M., Hamrouni, B., Bouguecha, S. and Dhahbi, M. (2004). Silica removal using ion-exchange resins. *Desalination*, *167*: 273-279.
- Benke, D.J., Wainwright, M.S., Nigam, K.D.P. and Rao, T.R. (2006). Kinetics of silica dissolution from rice husk char. *The Carnadian Journal of Chemical Engineering*, 84: 688-692.
- Bianchi, V.L.D., Moraes, I.O. and Capalbo, D.M.F. (2001). Fermentação em estado sólido. In: Biotecnologia industrial. São Paulo, Edgard Blücher, 2(13): 247-276.
- Blenke H, (1985) In Biotechnology:Fundamentals of Biochemical Engineering, Vol.2, Brauer, H (ed.) 466.
- Bobeck, G.E and Sue, H., The kinetics of dissolution of sphalerite in ferric chloride solution, *Metall. Trans.* 16 (B) (1985) 413–424.
- Bohart, G.S. and Adams, E.Q. (1920). Behavior of charcoal towards chlorine. *Journal of Chemical Society* 42:523–529.
- Bohart, G.S. and Adams, E.Q. (1920). Some aspect of the behaviour of charcoal with respect to chlown. *Journal of Chemical Society*. 42:523–544.
- Bridgeman, T.G., Darvell, L.I., Jones, J.M., William, P.T., Fahmi, R.Bridgewater, A.V., Barraclough, T., Shield, I., Yates, N., Thain, S.C. and Donnison, I.S. (2007). Influence of particle size on the analytical and chemical properties of two energy crops. *Fuel.* 86:60-72.
- Brozzoli, V., Bartocci, S., Terramoccia, S., Contò, G., Federici, F., D'Annibale, A. and Petruccioli, M. (2010). Stoned olive pomace fermentation with Pleurotus species and its evaluation as a possible animal feed. *Enzyme and Microbial Technology*, 46(3–4): 223-228.
- Buranov, A.U., and Mazza, G. (2008). "Lignin in straw of herbaceous crops," *Indusrial Crops Production*.28(3), 237-259.
- Bureenok, S., Suksombat, W. and Kawamoto, Y. (2011). Effects of the fermented juice of epiphytic lactic acid bacteria (FJLB) and molasses on digestibility and rumen fermentation characteristics of ruzigrass (Brachiaria ruziziensis) silages. *Livestock Science*. 138(1–3), 266-271.

- Busto, M. D., Ortega, N. and Perez-Mateos, M. (1996). Location, kinetics and stability of cellulases induced in *Trichoderma reesei* cultures. *Bioresource Technology*. *57*(2): 187-192.
- Cabrera, A., Cox, L., Spokas, K. U. R. T., Hermosín, M. C., Cornejo, J. and Koskinen, W. C. (2014). Influence of biochar amendments on the sorption–desorption of aminocyclopyrachlor, bentazone and pyraclostrobin pesticides to an agricultural soil. *Science of the Total Environment*. 470:438-443.
- Chaturvedi, V. and Verma, P. (2013). An overview of key pretreatment processes employed for bioconversion of lignocellulosic biomass into biofuels and value added products. *Biotechnology*, *3*(5):415–431.
- Chen, D. S., Zhao, L. S., Tao, Q. I., Hu, G. P., Zhao, H. X., Jie, L. I., and Wang, L. N. (2013). Desilication from titanium-vanadium slag by alkaline leaching. *Transactions of Nonferrous Metals Society of China*. 23(10):3076-3082.
- Chen, S., Yue, Q., Gao, B., Li, Q., Xu, X. and Fu, K. (2012). Adsorption of hexavalent chromium from aqueous solution by modified corn stalk: A fixed-bed column study. *Bioresource Technology*. 113:114–120.
- Chen, C.-C., Chuang, Y.-S., Lin, C.-Y., Lay, C.-H., and Sen, B. (2012). Thermophilic dark fermentation of untreated rice straw using mixed cultures for hydrogen production. *International Journal of Hydrogen Energy*. 37(20):15540-15546.
- Cheng, J., Su, H., Zhou, J., Song, W. and Cen, K. (2011). Microwave-assisted alkali pretreatment of rice straw to promote enzymatic hydrolysis and hydrogen production in dark- and photo-fermentation. *International Journal of Hydrogen Energy*. 36(3):2093-2101.
- Claudia, C. and Vassilis, I. (2014) *Progress in Filtration and Separation- Chapter* 10(Ion Exchange), Elsevier Ltd, 425-498.
- Correia, I., Nunes, A., Guedes, S., Barros, A. S. and Delgadillo, I. (2010). Screening of lactic acid bacteria potentially useful for sorghum fermentation. *Journal of Cereal Science*. 52(1):9-15.
- Correia, J. A. d. C., Júnior, J. E. M., Gonçalves, L. R. B. and Rocha, M. V. P. (2013). Alkaline hydrogen peroxide pretreatment of cashew apple bagasse for ethanol production: Study of parameters. *Bioresource Technology*. *139*:249-256.

- Csoka, L., Lorinecz, A., and Winkler, A. (2008). "Sonochemically modified wheat straw for pulp and papermaking to increase its economical performance and reduce environmental issues," *BioResources*. 3(1), 91-97.
- Curreli, N., Fadda, M.B., Rescigno, A., Rinaldi, A.C. and Soddu, A.G. (1997). Mild alkaline/oxidative pretreatment of wheat straw. *Process Biochemistry*. *32*(8): 665-670.
- de wilde, T., Mertens, J., Spanoghe, P., Ryckeboer, J., Jaeken, P. and Springael, D. (2008). Sorption kinetics and its effects on retention and leaching. *Chemosphere*. 72(3):509-516.
- Dubois, M., Gilles, K. Hamilton, J., Rebers, P. and Smith, F. (1956) Colometric method for determination of sugars and related substances. *Analytical Chemistry*. 28(3):350-356.
- Duchaine, C., Lavoie, M. C. and Cormier, Y. (1995). Effects of a Bacterial Hay Preservative (*Pediococcus pentosaceus*) on Hay under Experimental Storage Conditions. *Applied and Environmental Microbiology*, 61(12):4240-4243.
- Durot, N., Gaudard, F., and Kurek, B. (2003). The unmasking of lignin structures in wheat straw by alkali. *Phytochemistry*, 63(5), 617-623.
- Dutrizac, J.E., and MacDonald, R.J.C. (1978) The dissolution of sphalerite in ferric chloride solutions, *Metall. Trans.* 9 (B):543–551.
- El Sayed, H., A. E. El-Ashmawy and M. A. Hamad, (1979). "Waste Treatment and Utilization, Theory and Practices of Waste Management," *Procs. of the International Symposium, University of Waterloo*, ON 1978, M. Moo Young and G. J. Pergamon, Eds., Oxford, U.S. 363.
- Engasser, J.-M., Chamouleau, F., Chebil, L. and Ghoul, M. (2008). Kinetic modeling of glucose and fructose dissolution in 2-methyl 2-butanol. *Biochemical Engineering Journal*. 42(2):159-165.
- Fang, J., Matsuzaki, M., Suzuki, H., Cai, Y., Horiguchi, K., and Takahashi, T. (2012). Effects of lactic acid bacteria and urea treatment on fermentation quality, digestibility and ruminal fermentation of roll bale rice straw silage in wethers. *Japanese Society of Grassland Science*, 73-78.
- Fertani-Gmati, M., Brahim, K., Khattech, I., and Jemal, M. (2014). Thermochemistry and kinetics of silica dissolution in NaOH solutions: Effect of the alkali concentration. *Thermochimica Acta.* 594: 58-67.

- Filya, I., Ashbell, G., Hen, Y. and Weinberg, Z. G. (2000). The effect of bacterial inoculants on the fermentation and aerobic stability of whole crop wheat silage. *Animal Feed Science and Technology*, 88(1–2):39-46.
- Food and Agricultural Organization. (2016). Rice Market Monitor (Vol. 19, pp. 1-31): Trade and Market Division, Food and Agricultural Organization and United Nations.
- Freeman. (2000). Molecular cell biology, 4th edition. John Wiley &Sons. New York
- Gao, L., Yang, H., Wang, X., Huang, Z., Ishii, M., Igarashi, Y., and Cui, Z. (2008). Rice straw fermentation using lactic acid bacteria. *Bioresource Technology*, 99(8): 2742-2748.
- Galdeano, M.C. and Grossmann, M.V.E. (2005). Effects of treatment with alkaline hydrogen peroxide associated with extrusion on color and hydration properties of oat hulls. *Brazillian Archives of Biology and Technology*. 48(1):63-72.
- Gautam, R., Baral, S. and Herat, S. (2009). Biogas as a sustainable energy source in Nepal: Present status and future challenges. *Renewable and Sustainable Energy Reviews*. *13*(1):248-252.
- Gélinas, P. and Barrette, J. (2007). Protein enrichment of potato processing waste through yeast fermentation. *Bioresource Technology*. 98(5): 1138-1143.
- Gbor, P.K. (2003). Behaviour of Co, Ni, Cu and Fe during aqueous SO2 leaching of non-ferrous smelter slag. Ph.D. Thesis, University of Toronto, Toronto.
- Ghazali, H and Serin, T. (2015). *Manual Teknologi Penghasilan Silaj*. 1st Edition. MARDI. Kuala Lumpur.
- Ghribi, A. and Chlendi, M. (2011). Modelling of fixed bed Adsorption: Application to the Adsorption of organic dye. *Asian Journal of Textile*. 1(4):161-171.
- Goddard, J. S. and Perret, J. S. M. (2005). Co-drying fish silage for use in aquafeeds. *Animal Feed Science and Technology*, 118(3–4): 337-342.
- Godin, K.S. and G. Varani. (2013). SnoRNP biogenesis and function, in Post-transcriptional gene regulation. Wiley-Blackwell.
- Gopinath V., Meiswinkel T. M., Wendisch V. F. and Nampoothiri K. M. (2011). Amino acid production from rice straw and wheat bran hydrolysates by recombinant pentose-utilizing *Corynebacterium glutamicum*. *Application*. *Microbiology*. *Biotechnoogyl*. 92:985–996.

- Gowthaman, M.K., Krishna, C. and Moo-Young, M.(2001). Fungal solid state fermentation: an overview. *Applied Mycology and Biotechnology*. 1.305-312
- Gu, F., Wang, W., Jing, L. and Jin, Y. (2013). Effects of green liquor pretreatment on the chemical composition and enzymatic digestibility of rice straw. *Bioresource Technology*, 149(10):375-382.
- Gudavalli, R. K. P., Katsenovich, Y. P., Wellman, D. M., Idarraga, M., Lagos, L. E. and Tansel, B. (2013). Comparison of the kinetic rate law parameters for the dissolution of natural and synthetic autunite in the presence of aqueous bicarbonate ions. *Chemical Geology.351*: 299-309.
- Gupta, V.K. and Langar, P.N. (1988). Pleurotus florida for upgrading the nutritive value of wheat straw. *Biological Wastes*. 23: 57-64.
- Golshan-Shirazi, S. and Guichon, G. (1991). Combined effects of finite axial dispersion and slow adsorption / desorption kinetics on band profiles in non-linear Chromatography. *Journal of Physical Chemistry*. 95: 6390-6395
- Gregory, K.F. (1982). Feed enrichment with microbial protein. *Conservation Recycle*. 5:33-40.
- Gu, F., Wang, W., Jing, L. and Jin, Y. (2013). Effects of green liquor pretreatment on the chemical composition and enzymatic digestibility of rice straw. *Bioresource Technology.* 149(0): 375-382.
- Gudavalli, R., Y. Katsenovich, D. Wellman, M. Idarraga, L. Lagos, and B. Tansel (2013). Comparison of the kinetic rate law parameters for the dissolution of natural and synthetic autunite in the presence of aqueous bicarbonate ions. *Chemical Geology*. 351:299–309.
- Gupta, V. K. and Suhas. (2009). Application of low-cost adsorbents for dye removal

 A review. *Journal of Environmental Management*. 90(8):2313-2342.
- Hammel, K.E., Kapich, A.N., Jensen, K.A., and Ryan, Z.C. (2002). Reactive oxygen species as agents of wood decay by fungi. *Enzymatic Microbology Technology* .30(4):445–453.
- Han, G., Deng, J., Zhang, S., Bicho, P. and Wu, Q. (2010). Effect of steam explosion treatment on characteristics of wheat straw. *Industrial Crops and Products*, 31(1):28-33.
- Heap, J.T., Kuehne, S.A., Ehsaan, M., Cartman, S.T., Cooksley, C.M., Scott, J.C. and Minton, N.P.,(2010). The ClosTron: Mutagenesis in Clostridium refined and streamlined. *Journal of Microbiology. Methods*. 80:49-55.

- Heimann, R.B.Classic and advanced ceramics, Wiley.com, 2010.
- Helgeson, H. C., Murphy, W. M. and Aagaard, P.(1984). Thermodynamic and kinetic constrains on reaction rates among minerals and aqueous solutions. II.
 Rate constants, effective surface area, and the hydrolysis of feldspar.
 Geochim. Cosmochim. Acta 48: 2405-2432.
- Hodaifa, G., Alami, S.B.D., Ochando-Pulido, J.M. and Víctor-Ortega, M.D.(2014). Iron removal from liquid effluents by olive stones on adsorption column: breakthrough curves. *Ecological. Engineering*. 73: 270-275.
- Hölker, U. and Lenz, J. (2005). *Solid-State Fermentation Are There Any Biotechnological Advantages?* Current Opinion Microbiology, Vol. 8, pp. 301–306.
- Holzer, M., Mayrhuber, E., Danner, H. and Braun, R. (2003). The role of *Lactobacillus buchneri* in forage preservation. *TRENDS in Biotechnology*, 282-287.
- Horn, C. H., du Preez, J. C. and Lategan, P. M. (1988). Protein enrichment of banana plant wastes by yeast cultivation. *Biological Wastes*. 24(2): 127-136
- Hsu, P.-K., Liu, C.-P., Liu, L.-Y., Chang, C.-H. and Yang, S.-S. (2013). Protein enrichment and digestion improvement of napiergrass and pangolagrass with solid-state fermentation. *Journal of Microbiology, Immunology and Infection*, 46(3): 171-179.
- Hu, C.-C., Liu, L.-Y. and Yang, S.-S. (2012). Protein enrichment, cellulase production and in vitro digestion improvement of pangolagrass with solid state fermentation. *Journal of Microbiology, Immunology and Infection*, 45(1): 7-14.
- Hu, C., Yen, A., Joshi, N. and Hartman, R. L. (2016). Packed-bed microreactors for understanding of the dissolution kinetics and mechanisms of asphaltenes in xylenes. *Chemical Engineering Science*, 140: 144-152.
- Huang, G., Shi, J. X. and Langrish, T. A. G. (2007). NH4OH–KOH pulping mechanisms and kinetics of rice straw. *Bioresource Technology*. 98(6): 1218-1223.
- Ibrahim, F. S., Babiker, E. E., Yousif, N. E. and El Tinay, A. H. (2005). Effect of fermentation on biochemical and sensory characteristics of sorghum flour supplemented with whey protein. *Food Chemistry*, 92(2): 285-292.

- Icenhower, J. P., and Dove, P. M. (2000). The dissolution kinetics of amorphous silica into sodium chloride solutions: effects of temperature and ionic strength. *Geochimica et Cosmochimica Acta*, 64(24): 4193-4203.
- Iler, R.K. (1979). The Chemistry of Silica. John Wiley &Sons. New York
- Irfan, M., Gulsher, M., Abbas, S., Syed, M., Nadeem, M. and Baig S. (2011). Effects of various pretreatment conditions on enzymatic saccharification. Songkalanakarin Journal of Science and Technology. 33(4):397-404.
- Jahan, M. S., Haris, F., Rahman, M. M., Samaddar, P. R., and Sutradhar, S. (2016).
 Potassium hydroxide pulping of rice straw in biorefinery initiatives. *Bioresource Technology*, 219:445-450.
- Jian-Xin, L., Wang, X. and Shi, Z. (2001). Addition of rice straw or/and wheat bran on composition, ruminal degradability and voluntary intake of bamboo shoot shell silage fed to sheep. *Animal Feed Science and Technology*, 129-138.
- Karagöz, P., Rocha, I.V., Ozkan, M. and Angelidaki, I. (2012). Alkaline peroxide pretreatment of rapeseed straw for enhancing bioethanol production by same vessel saccharification and co-fermentation. *Bioresource Technology*. 104: 348-357.
- Karimi, K., Edebo, L. and Taherzadeh, M. J. (2008). Mucor indicus as a biofilter and fermenting organism in continuous ethanol production from lignocellulosic hydrolyzate. *Biochemical Engineering Journal*. *39*(2): 383-388.
- Karunanandaa, K., Varga, G.A., Akin, D.E., Rigsby, L.L. and Royse, D.J. (1995).
 Botanical fractions of rice straw colonized by white-rot fungi: Changes in chemical composition and structure. *Animal. Feed Science and Technology*. 55:179–199.
- Karunanandaa, K. and Varga, G.A. (1996). Colonization of crop residues by white-rot fungi: cell wall monosaccharides, phenolic acids, ruminal fermentation characteristics and digestibility of cell wall fiber components in vitro. *Animal Feed Science and. Technology.* 63: 273–288.
- Kewalramani, N., Kamra, D.N., Lall, D. and Pathak, N.N. (1988). Bioconversion of sugarcane bagasse with white rot fungi. *Biotechnology. Letter*. 10: 369–372.
- Khalili, H., Sairanen, A., Nousiainen, J. and Huhtanen, P. (2005). Effects of silage made from primary or regrowth grass and protein supplementation on dairy cow performance. *Livestock Production Science*, 96(2–3): 269-278.

- Khamis, A.K., Asli, U.A., Zailani, S.N., Brown, O.R., Zakaria, Z.A. and Razali, F. (2014). Magnesium desorption in utisols soils treated by Rhodopseudomonal Palustric bacterium. *International Jounal of Advance in Chemical Engineering & Biological Science*. 1(2):158-161.
- Khan, M. M. R., Rahman, M. W., Mozumder, M. S. I., Ferdous, K., Ong, H. R., Chan, K. M. and Prasad, D. R. (2016). Performance of a submerged adsorption column compared with conventional fixed-bed adsorption. *Desalination and Water Treatment*, 57(21): 9705-9717.
- Kim, S. C., Adesogan, A. T., Kim, J. H. and Ko, Y. D. (2006). Influence of replacing rice straw with wormwood (*Artemisia montana*) silage on feed intake, digestibility and ruminal fermentation characteristics of sheep. *Animal Feed Science and Technology*. 128(1–2): 1-13.
- Kim, B.H. and Gadd, G.M (2008) *Bacterial physiology and metabolism*. Cambridge University Press, Cambridge, 529pp
- Kim, T. and Buratowski, S. (2009) Dimethylation of H3K4 by Set1 recruits the Set3 histone deacetylase complex to 5' transcribed regions. *Cell* .137(2):259-72
- Klason, P. (1961). *In Method of wood chemistry*. Vol 2. Browning Interscience Sons, 785-799.
- Kofa, G. P., NdiKoungou, S., Kayem, G. J. and Kamga, R. (2015). Adsorption of arsenic by natural pozzolan in a fixed bed: Determination of operating conditions and modeling. *Journal of Water Process Engineering*. 6:166-173.
- Kumar, S., and Gomes, J., (2008). Performance evaluation of reactors designed for bioconversion of wheat straw to animal feed. *Anim. Feed Sci. Technol.* 144, 149–166.
- Kovács K, Szakacs G, and Zacchi G.(2009). Comperative enzymatic hydrolysis of pretreated spruce by supernatants, whole fermentation broths and washed mycelia of Trichoderma reesei and Trichoderma atroviride. *Bioresource Technology*. 100:1350-1357.
- Kumar, U., and Bandyopadhyay, M. (2006). Sorption of cadmium from aqueous solution using pretreated rice husk. *Bioresource Technology*, 97(1), 104-109.
- Kumar, P.,Barrett, D.M.,Delwiche, M.J. and Stroeve, P. (2009), Methods of pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production *Industrial Engineering Chemical Resource*. 48:3713–3729.

- Kumar, G., Lay, C.-H., Chu, C.-Y., Wu, J.-H., Lee, S.-C. and Lin, C.-Y. (2012).
 Seed inocula for biohydrogen production from biodiesel solid residues. *International Journal of Hydrogen Energy*. 37(20): 15489-15495.
- Lee, S., Tran, T., Park, Y., Kim, S. And Kim, M.(2006). Study on the kinetics of iron oxide leaching by oxalic acid. *International Journal of Mineral Process*. 80: 144–152.
- Levenspiel O. 1972 Chemical reaction engineering, 2nd ed.; Wiley: New York,
- Levenspiel, O. 1999. *Chemical Reaction Engineering*, 3rd Edition. Wiley, New York.
- Li, Y., Peng, X. and Chen, H. (2013). Comparative characterization of proteins secreted by Neurospora sitophila in solid-state and submerged fermentation. *Journal of Bioscience and Bioengineering*. 116(4):493-498.
- Liddell, K.C. (2005). Shrinking core models in hydrometallurgy: what students are not being told about the pseudo-steady approximation. *Hydrometallurgy* 79: 62–68.
- Lima, R., Lourence, M., Díaz, R. F., Castro, A. and Fievez, V. (2010). Effect of combined ensiling of sorghum and soybean with or without molasses and lactobacilli on silage quality and in vitro rumen fermentation. *Animal Feed Science and Technology*. 122-131.
- Liu, Y., Qi, T., Chu, J., Tong, Q. And Zhang, Y. (2006). Decomposition of ilmenite by concentrated KOH solution under atmospheric pressure. *International Journal Miner Process*. 81:79–84
- Lydersen, A. L. *Mass transfer in engineering practice*, John Wiley & Sons, April 1983, 321
- Liu, J.-X., J.-A. Ye, and H.-W. Ye. (1998) The effects of supplementary Chinese milk vetch silage on the growth rate of cattle and their intake of ammoniated rice straw. *Animal Feed Science and Technology*. **65**(1): p. 79-86.
- Liu, J.-X., Orskov, E. R., and Chen, X. B. (1999). Optimization of steam treatment as a method for upgrading rice straw as feeds. *Animal Feed Science and Technology*, 76(3–4):345-357.
- Liu, J. X., Yao, J., Yan, B., Yu, J. Q. and Shi, Z. Q. (2001). Effects of mulberry leaves to replace rapeseed meal on performance of sheep feeding on ammoniated rice straw diet. *Small Ruminant Research*, 39(2): 131-136.

- Mahbod, S., Mohamed M.H., Abdullah, S.N.A. (2015). Importance of Silicon and Mechanisms of Biosilica Formation in Plants. *BioMed Research International*. 1-16.
- Mandavgane, S.A., Paradkar, G.D., Varu, J., Pamar, R., and Subramanian, D. (2007). Desilication of agrobased black liquor and green liquor using jet loop reactor. *Indian Journal of Chemical Technology*, *14*: 606-610.
- Manivannan, R. and Ramanathan, S. (2009). The effect of hydrogen peroxide on polishing removal rate in CMP with various abrasives. *Applied Surface Science*, 255(6): 3764-3768.
- Martin, M.A. (1991). *Bioconversion of waste materials to industrial products*. Elsevier Applied science, London, UK. Pp. 44 190.
- Martínez-Cuesta, M. C., Fernández de Palencia, P., Requena, T.and Peláez, C., (1998). Enhancement of proteolysis by a *Lactococcus lactis* bacteriocin producer in a cheese model system. *Journal of Agricultural and Food Chemistry* 46:3863–3867.
- Mecfel, J., Hinke, S., Goedel, W. A., Marx, G., Fehlhaber, R., Bäucker, E. and Wienhaus, O. (2007). Effect of silicon fertilizers on Si accumulation in wheat. *Journal of Plant Nutrition and Soil Science* 170:769-772.
- Meeske, R. and Basson, H. M. (1998). The effect of a lactic acid bacterial inoculant on maize silage. *Animal Feed Science and Technology*, 70(3): 239-247.
- Meyreles, L. and Preston, T. R. (1977). The banana plant as cattle feed: Effect of different levels of banana leaves on voluntary intake of chopped sugar cane stalk. *Tropical Animal Production*. 3:229-233.
- Mission, M., Haron, R., Ahmad, M.F., Kamaroddin. and Amin, N.A.S. (2009). Pretreatment of empty palm fruit bunch for lignin degradation. *Jurnal Teknologi*. 50:89-98.
- Mohd-Setapar, S. H., Abd-Talib, N. and Aziz, R. (2012). Review on crucial parameters of silage quality. *APCBEE Procedia*, *3*(0), 99-103.
- Mohammadzadeh, H., Khorvash, M., Ghorbani, G. R. and Yang, W. Z. (2012). Frosted corn silage with or without bacterial inoculants in dairy cattle ration. *Livestock Science*. 153-159.
- Moo-Young, M., Chisti, Y. and Vlach, D.(1992). Fermentative conversion of cellulosic substrates to microbial protein by *Neuorospora sitophila*. *Biotechnology Letters*. 14(9): 863-868

- Moyson, E. and Verachart, H.(1991). Growth of higher fungi on wheat straw and their impact on the digestibility of the substrate. *Applied. Microbiology*. *Biotechnology*. 36:42–424.
- Nader, G. A. and Robinson, P. H. (2008). Effects of maceration of rice straw on voluntary intake and performance of growing beef cattle fed rice straw-based rations. *Animal Feed Science and Technology*, *146*(1–2):74-86.
- Nasseri, A.T., Rasoul-Amini, S., Moromvat, M.H. and Ghasemi, Y. (2011). Production of single cell protein from fruits waste. *Am. J. Food Technol.*, 6(2): 103.
- Nayl, A. A., Awwad, N. S. and Aly, H. F. (2009). Kinetics of acid leaching of ilmenite decomposed by KOH: Part 2. Leaching by H₂SO₄ and C₂H₂O₄. *Journal of Hazardous Materials*, 168(2–3): 793-799.
- Nkosi, B. D. and Meeske, R. (2010). Effects of ensiling totally mixed potato hash ration with or without a heterofermentative bacterial inoculant on silage fermentation, aerobic stability, growth performance and digestibility in lambs. *Animal Feed Science and Technology*, 161(1–2): 38-48.
- Nurfeta, A., Tolera, A., Eik, L. O. And Sundstøl, F. (2009). Effect of enset (Ensete ventricosum) leaf supplementation on feed intake, digestibility, nitrogen utilization and body weight gain of sheep fed untreated or urea and calcium oxide-treated wheat straw. *Livestock Science*.122(2–3): 134-142.
- O'Mara, F. P., Fitzgerald, J. J., Murphy, J. J. and Rath, M. (1998). The effect on milk production of replacing grass silage with maize silage in the diet of dairy cows. *Livestock Production Science*. 55(1): 79-87.
- Oberoi, H. S., Vadlani, P. V., Brijwani, K., Bhargav, V. K. and Patil, R. T. (2010). Enhanced ethanol production via fermentation of rice straw with hydrolysate-adapted *Candida tropicalis* ATCC 13803. *Process Biochemistry*. 45(8): 1299-1306
- Oguntimein, G. and Moo-Young, M. (1991). Production and properties of β-glucosidases by *Neurospora sitophila*. World Journal of Microbiology and Biotechnology 7:4–11.
- Oguntimein, G., Vlach, D. and Moo-Young, M. (1992). Production of cellulolytic enzymes by *Neurospora sitophila* grown on cellulosic materials. *Bioresource Technology*. *39*(3):277-283

- Oguz, E. and Ersoy, M. (2010). Removal of Cu2+ from aqueous solution by adsorption in a fixed bed column and neural network modeling. *Chemical Engineering Journal*. 164 (1):56–62.
- Okano, K., Iida, Y., Samsuri, M., Prasetya, B., Usagawa, T. and Watanabe, T. (2006). Comparison of in vitro digestibility and chemical composition among sugarcane bagasses treated by four white-rot fungi. *Animal. Science. Journal* 77:308–313.
- Okano, K., Ohkoshi, N., Nishiyama, A., Usagawa, T. and Kitagawa, M., (2009). Improving the nutritive value of madake bamboo, *Phyllostachys bambusoides*, for ruminants by culturing with the white-rot fungus *Ceriporiopsis subvermispora*. *Animal. Feed Science*. *Technology*. 152:278–285.
- Okine, A., Hanada, M., Aibibula, Y. and Okamoto, M. (2005). Ensiling of potato pulp with or without bacterial inoculants and its effect on fermentation quality, nutrient composition and nutritive value. *Animal Feed Science and Technology*. 121(3–4): 329-343.
- Pandey, A.; Soccol, C.R. and Mitchell, D. (2000). New Developments in Solid State Fermentation: I- *Bioprocesses and Products. Process Biochemistry*. 35(10): 1153-1169.
- Pandey, A., Negi, S., Binod, P. and Larroche, C. (2014). *Pretreatment of Biomass: Process and Technology*. Academic Press, 35 (10): 1153-1169.
- Patel, M.M. and Bhatt, R.M. (1992). Optimization of the alkaline peroxide pretreatment for the delignification of rice straw and its applications. *Journal of Chemical Technology and Biotechnology*. 53:253-263
- Peckam, G.D. and Naught, J. M. (1992). Applications of Maxwell-Boltzmann distribution diagram. *Journal of Chemical Education*. 69 (7): 554
- Pedersen, M., Viksø-Nielsen, A., and Meyer, A. S. (2010). Monosaccharide yields and lignin removal from wheat straw in response to catalyst type and pH during mild thermal pretreatment. *Process Biochemistry*. 45(7):1181-1186
- Pekarovic, J. (2005). Desilication of agricultural residues- the first step prior to pulping. *Appita Journal*. 58(2):130-134
- Perkins, D. D. and Davis, R. H. (2000). Evidence for Safety of Neurospora Species for Academic and Commercial Uses. *Applied and Environmental Microbiology*. 66(12): 5107-5109.

- Pessoa, Jr A., Manchila, I.M. and Sato, S.(1996). Cultivation of *Candida tropicalis* in sugar cane bagasse hemicellulose hydrolysate for microbial protein production. *Journal of Biotechnology*. 51: 83-88.
- Pieper, R., Hackl, W., Korn, U., Zeyner, A., Souffrant, W. and Pieper, B. (2011). Effect of ensiling triticale, barley and wheat grains at different moisture content and addition of *Lactobacillus plantarum* (DSMZ 8866 and 8862) on fermentation characteristics and nutrient digestibility in pigs. *Animal Feed Science and Technology*. 96-105.
- Rabelo, S. C., Carrere, H., Maciel Filho, R. and Costa, A. C. (2011). Production of bioethanol, methane and heat from sugarcane bagasse in a biorefinery concept. *Bioresource Technology*. *102*(17): 7887-7895.
- Rahal, A., Singh, A. and Singh, M. (1997). Effect of urea treatment and diet composition on, and prediction of nutritive value of rice straw of different cultivars. *Animal Feed Science and Technology*. 68(1–2): 165-182.
- Rahman, M.M., Lourenço, M., Hassim, H.A., Baars, J.J.P., Sonnenberg, A.S.M., Cone, J.W., De -Boever, J. And Fievez, V. (2011). Improving ruminal degradability of oil palm fronds using white rot fungi. *Animal. Feed Science Technology*. 169:157–166.
- Rahman, S.U and Al-Saleh, M.A. (1999) "Kinetic study of leaching process of Raney silver catalyst", *Chemical Engineering Journal*, 72(3):229-233.
- Rahmat, H., Hodge, R. A., Manderson, G. J., & Yu, P. L. (1995). Solid-substrate fermentation of Kloeckera apiculata and Candida utilis on apple pomace to produce an improved stock-feed. *World Journal of Microbiology and Biotechnology*, 11(2):168-170.
- Raju, R. A. and Reddy, M. N. (2000) Integrated management of green leaf, compost, crop-residues and inorganic fertilizers in rice (Oryza sativa) –rice system. *Indian Journal of Agronomy* 45: 629 -635
- Ranjan, A. and Moholkar, V. S. Comparative study of various pretreatment techniques for rice straw saccharification for the production of alcoholic biofuels. *Fuel*(0).
- Rasoul-Amini, S., Montazeri-Najafabady, N., Mobasher, M. A., Hoseini-Alhashemi, S. and Ghasemi, Y. (2011). *Chlorella* sp.: A new strain with highly saturated fatty acids for biodiesel production in bubble-column photobioreactor. *Applied Energy*, 88(10):3354-3356.

- Rath P.C., Paramguru, R.K. and Jena P.K, (1988) Kinetics of dissolution of sulphide minerals in ferric chloride solution. Part 2: application to complex sulphide concentrates, *Trans. Inst. Miner. Metall. Sect. C Miner. Process. Extr. Metall.* 97:150–158.
- Rehman, M. S. U., Umer, M. A., Rashid, N., Kim, I. and Han, J.-I. (2013). Sono-assisted sulfuric acid process for economical recovery of fermentable sugars and mesoporous pure silica.
- Rimer, J.D., Trofymluk, O., Navrotsky, A., Lobo, R.F. and Vlachos, D.G. (2007). Kinetic and thermodynamic studies of silica nanoparticle dissolution, *Chemical. Materials.* 19:4189–4197.
- Rodriduez-Martinez, C.A., Gonzales-Acevado, Z.I., Olguin, M.T. and Frias-Palos, H. (2014). Adsorption and Desorption of selenium by teo non-living biomasses of aquatic weeds at dynamics conditions. *Clean Energy Environment Policy*.
- Rozada, F.M., Otero, A.I. and Movani, A. (2007). Application in fixed bed systems of adsorbents obtained from sludge and discarded tyres. *Dyes Pigmentation*. 72: 47-56
- Sadrzadeh, M., Ghadimi, A. and Mohammadi, T. (2009). Coupling a mathematical and a fuzzy logic-based model for prediction of zinc ions separation from wastewater using electrodialysis. *Chemical Engineering Journal*. *151*(1–3): 262-274.
- Safari, V., Arzpeyma, G., Rashchi, F., and Mostouf, N. (2009). A shrinking particle–shrinking core model for leaching of a zinc ore containing silica. *International Journal of Mineral Processing*.93:79–83
- Safarzadeh, M. S., Moradkhani, D., and Ojaghi-Ilkhchi, M. (2009). Kinetics of sulfuric acid leaching of cadmium from Cd–Ni zinc plant residues. *Journal of Hazardous Materials*, 163(2–3): 880-890.
- Saha, B.C. and Cotta, M. A. (2006). Ethanol production from alkaline peroxide pretreated enzymatically saccharified wheat straw. *Biotechnology Prog.* 22: 449-453.
- Sahebi M., Hanafi M. M., Akmar A. S., Rafii M. Y., Azizi P. and Tengoua F. F.. (2015). Importance of silicon and mechanisms of biosilica formation in plants. *BioMed Res. Int*.1–16.
- Sakurai, Y., Lee, T.H. and Shiota, H. On the convenient method for glucosamine estimation in koji. *Agriculture Biotechnology Chemical*. 41(4): 619-624.

- Salmimies, R., Mannila, M., Kallas, J. and Hakkinen, A.(2012) Acidic dissolution of hematite: kinetic and thermodynamic investigations with oxalic acid. *International Journal of Mineral Processing*.110–111:121–125
- Sánchez, C. (2009). Lignocellulosic residues: Biodegradation and bioconversion by fungi. *Biotechnology*. *Advances*. 27:85-194.
- Sarin, V., Singh, T.S. and Pant, K.K. (2006) Thermodynamic and breakthrough column studies for the selective sorption of chromium from industrial effluent on activated eucalyptus bark. *Bioresource*. *Technology*. 97(16):1986–1993.
- Santos, M.M.; Rosa, A.S.; Dal'boit, S.; Mitchell, D.A. and Kriger, N.(2004) Thermal Denaturation: Is Solid-State Fermentation Really a Good Technology for the Production of Enzymes? *Bioresource Technology*, 93(3), 261-268.
- Schroeder, J. W. (2004). *Silage Fermentation and Preservation*. Extension Dairy Specialist. North Dakota State University. South Dakota.
- Schmidt, C. G. and Furlong, E. B. (2012). Effect of particle size and ammonium sulfate concentration on rice bran fermentation with the fungus Rhizopus oryzae. *Bioresource Technology*, 123(0):36-41.
- Seidel, A., Löbbus, M., Vogelsberger, W., and Sonnefeld, J. (1997). The kinetics of dissolution of silica 'Monospher'into water at different concentrations of background electrolyte. *Solid State Ionics*, *101*:713-719.
- Sharma, R.K. and Arora, D.S., (2010). Production of lignocellulolytic enzymes and enhancement of in vitro digestibility during solid state fermentation of wheat straw by *Phlebia floridensis*. *Bioresource*. *Technology*. 101:9248–9253.
- Shojaosadati, S. A., Faraidouni, R., Madadi-Nouei, A. and Mohamadpour, I. (1999). Protein enrichment of lignocellulosic substrates by solid state fermentation using *Neurospora sitophila*. *Resources, Conservation and Recycling, 27*(1–2): 73-87.
- Shaw, D. E. (1998). Species of *Neurospora* recorded in Australia, and the collection of Neurospora conidia by honey bees in lieu of pollen. *Mycologist.* 12(4): 154-158
- Shawky, B. T., Mahmoud, M. G., Ghazy, E. A., Asker, M. M. S. and Ibrahim, G. S. (2011). Enzymatic hydrolysis of rice straw and corn stalks for monosugars production. *Journal of Genetic Engineering and Biotechnology*. *9*(1): 59-63.
- Shinozaki, Y. and Kitamoto, H. K. (2011). Ethanol production from ensiled rice straw and whole-crop silage by the simultaneous enzymatic saccharification

- and fermentation process. *Journal of Bioscience and Bioengineering*. 111(3): 320-325.
- Shen, H. S., Ni, D. B., and Sundstøl, F. (1998). Studies on untreated and urea-treated rice straw from three cultivation seasons: 1. Physical and chemical measurements in straw and straw fractions. *Animal Feed Science and Technology*. 73(3–4):243-261.
- Sherief, A.A., El-Tanash, A.B. and Temraz, A.M. (2010). Lignocellulolytic enzymes and substrate utilization during growth and fruiting of Pleurotus ostreatus on some solid wastes. *Journal of Environmental. Science and Technology*. 3: 18–34.
- Shinozaki, Y. and Kitamoto, H. K. (2011). Ethanol production from ensiled rice straw and whole-crop silage by the simultaneous enzymatic saccharification and fermentation process. *Journal of Bioscience and Bioengineering*. 111(3): 320-325
- Shrivastava, B., Nandal, P., Sharma, A., Jain, K. K., Khasa, Y. P., Das, T. K. and Kuhad, R. C. (2012). Solid state bioconversion of wheat straw into digestible and nutritive ruminant feed by *Ganoderma* sp. rckk02. *Bioresource Technology*, 107(0): 347-351.
- Sinitsyn, A. P., Gusakov, A.V. and Vlasenko, E.Y. (1991) .Effect of structural and physico-chemical features of cellulosic substrates on the efficiency of enzymatic hydrolysis. Applied. Biochemical and Biotechnology. 30:43–59
- Slater, M. J. Principal of Ion Exchange Technology, Elsevier Ltd, 1991.
- Smith GS, Nelson AB, Boggino EJ. Digestibility of forages *in vitro* as affected by content of "silica" *Journal of Animal Science*. 1971;33:466–471.
- Soil Management Division, (2014). *Paddy +Statistics of Malaysia 2013* 1st Edition. Department of Agriculture, Kuala Lumpur.
- Soodeen-Karamath, S. and Youssef, F. G. (1999). Effect of monensin, avoparcin and grass supplementation on utilization of urea-treated rice straw by sheep and goats. *Small Ruminant Research*. *33*(3): 201-211.
- Sommart, K., Parker, D. S., Rowlinson, P. and Wanapat, M. (1999). Fermentation characteristics and microbial protein synthesis in an in vitro system using cassava, rice straw and dried ruzi grass as substrate. *Ruminal Microbial Protein Synthesis & Fermentation End Product*. 1084-1093.

- Souza, C. H. B. and Saad, S. M. I. (2009). Viability of *Lactobacillus acidophilus* La-5 added solely or in co-culture with a yoghurt starter culture and implications on physico-chemical and related properties of Minas fresh cheese during storage. *LWT Food Science and Technology*. 42(2): 633-640.
- Su, Y., Du, R., Guo, H., Cao, M., Wu, Q., Su, R. And He, Z. (2015). Fractional pretreatment of lignocellulose by alkaline hydrogen peroxide: Characterization of its major components. *Food and Bioproducts Processing*, 94:322-330.
- Su, Y., Wei, Z., Zhao, G., Yan, C. and Lin, S. (2012). Mutation of Cellulose Synthase Gene Improves the Nutritive Value of Rice Straw. Asian-Australia *Journal of Animal Science*, 800-805.
- Sue, H. Ph.D. Thesis, University of Idaho, Moscow, ID, 1976
- Subbaiah, M.V., Yuvaraja, G. and Vijaya, Y. (2011). Equilibrium, kinetic and thermodynamic studies on biosorption of Pb (II) and Cd (II) from aqueous solution by fungus (Trametes versicolor) biomass. *Journal of Taiwan Institute Chemical Engineering*. 42 (6):965–971.
- Sun, R. C., Tomkinson, J., Wang, Y. X., and Xiao, B. (2000). Physico-chemical and structural characterization of hemicelluloses from wheat straw by alkaline peroxide extraction. *Polymer*, *41*(7): 2647-2656.
- Sun, Y., and Cheng, J.(2002). Hydrolysis of lignocellulosic materials for ethanol production: a review. *Bioresource Technology*.83.1-11.
- Suzuki, Y., Okano, K., and Kato, S., (1995). Characteristics of white-rotted woody materials obtained from Shiitake mushroom (*Lentinus edodes*) and nameko mushroom (*Pholiota nameko*) cultivation with in vitro rumen fermentation. *Animal. Feed Science and. Technology.* 66: 406–411.
- Swain, M. R. and Krishnan, C. (2015). Improved conversion of rice straw to ethanol and xylitol by combination of moderate temperature ammonia pretreatment and sequential fermentation using *Candida tropicalis*. *Industrial Crops and Products*. 77:1039-1046.
- Szubert, A., Łupiński, M. and Sadowski, Z., (2006). Application of shrinking core model to bioleaching of black shale particles. *Physicochem. Prob. Miner. Process*, 40:211–225.
- Szymczycha-Madeja, A., (2011). Kinetics of Mo, Ni, V and Al leaching from a spent

- hydrodesulphurization catalyst in a solution containing oxalic acid and hydrogen peroxide. Journal of Hazard Materials. 186 (2–3), 2157–2161.
- Taherzadeh, M. J., and Karimi, K. (2008). "Pretreatment of lignocellulosic wastes to improve ethanol and biogas production: A review," International Journal of Molecular Sciece .9, 1621-1651.
- Tamai, K. and Ma, J.F. (2003). Characterization of silicon uptake by rice roots. *New Phytologist*, 158:431-436.
- Tamaki, Y. and Mazza, G. (2010). Measurement of structural carbohydrates, lignins and micro-components of straw and shives :Effects of extractives, particle sizes and crop species. *Industrial Crops and Products*. 31:534-541.
- Tentratian, M.L. and Fields.(1990) Enrichment of ground corncobs with cellulolytic microorganisms. *Biological Wastes*, 34: 123–131.
- Terry, B. and Monhemius, A. J.(1983) Acid dissolution of willemite ((Zn, Mn)₂ SiO₄) and hemimorphite Zn₄Si₂O₇(OH)₂.H₂O. *Metallurgical and Materials Transactions B* .14(3): 335–346.
- Thanikachalam, A. and Rangarajan, M. (1986). Protein enrichment of rice straw by fermentation with *Cellulomonas* sp. *Agricultural Wastes*, *15*(3):215-224
- Thomas, H.C., (1944). Heterogeneous ion exchange in a flowing system. *Journal of American Chemistry Society*. 66:1466–1664.
- Thygesen, A., Thomsen, A. B., Schmidt, A. S., Jorgensen, H., Ahring, B. K. and Olsson, L. (2003). Production of cellulose and hemicellulose-degrading enzymes by filamentous fungi cultivated on wet-oxidised wheat straw. *Enzyme and Mirobial Technology*. 32: 606-615.
- Trinh, T.T., Jansen, A.P.J. and van Santen, R.A. (2006) Mechanism of oligomerisation reactions of silica. *Journal of Physical Chemistry B* 110: 23099–23106.
- Tripathi, J. P. and J. S. Yadav. (1992). Optimization of solid-state fermentation of wheat straw in to animal feed by *Pleurotus ostreatus*: A pilot effort. *Animal. Feed Science and. Technology*. 37:59-72.
- Turner, B. C., Perkins, D. D. and Fairfield, A. (2001). Neurospora from natural populations: A global study. *Fungal Genetics and Biology*, *32*(2): 67-92.
- Tuyen, D. V., Phuong, H. N., Cone, J. W., Baars, J. J. P., Sonnenberg, A. S. M., and Hendriks, W. H. (2013). Effect of fungal treatments of fibrous agricultural

- by-products on chemical composition and in vitro rumen fermentation and methane production. *Bioresource Technology*, 129(0):256-263.
- Ugwuanyi, J. O., Harvey, L. M. and McNeil, B. (2008). Protein enrichment of corn cob heteroxylan waste slurry by thermophilic aerobic digestion using Bacillus stearothermophilus. *Bioresource Technology*, *99*(15): 6974-6985.
- Vadiveloo, J. (2003). The effect of agronomic improvement and urea treatment on the nutritional value of Malaysian rice straw varieties. *Animal Feed Science* and Technology, 133–146.
- Van Soest, P. J. (2006). Rice straw, the role of silica and treatments to improve quality. *Animal Feed Science and Technology*, 130(3–4):137-171.
- Van Eylen, D., van Dongen, F., Kabel, M. and de Bont, J. (2011). Corn fiber, cobs and stover: Enzyme-aided saccharification and co-fermentation after dilute acid pretreatment. *Bioresource Technology*, 102(10):5995-6004
- Viniegra-Gonzalez, G.; Favela-Torres, E.; Noe Aguilar, C.; Jesus Romero-Gomez, J.; DiazGodinez, G. and Augur, C. (2003). Advantages of fungal enzyme production in solid state over liquid fermentation systems. *Biochemical and Engeneering Journal*.13:157–167.
- Vogelsbagar, W., Seidel, A. and Rudaoff, Q. (1997). Solubility of silica gel in water. *Journal of Chemical Society. Faraday T.* 88:473-476
- Wanapat, M., Polyorach, S., Chanthakhoun, V. and Sornsongnern, N. (2011). Yeast-fermented cassava chip protein (YEFECAP) concentrate for lactating dairy cows fed on urea–lime treated rice straw. *Livestock Science*. 258–263.
- Wang, C., Duan, X., Wang, W., Li, Z., and Qin, Y. (2012). Establishment and verification of a shrinking core model for dilute acid hydrolysis of lignocellulose. *Frontiers in Energy*, 6(4):413-419.
- Wang, M., Zhao, X. G., Liao, H. Y., Tan, Z. L., Tang, S. X. and Sun, Z. H. (2011). Effects of rice straw particle size on digesta particle size distribution, nitrogen metabolism, blood biochemical parameters, microbial amino acid composition and intestinal amino acid digestibility in goats. *Animal Science Journal*, 78–85.
- Ware, R., and Zinn, R. (2005). Effect of pelletizing on the feeding value of rice straw in steam-flaked corn growing-finishing diets for feedlot cattle. *Animal Feed Science and Technology*. 631-642.

- Weimer, P., Mertens, D., Ponnampalan, E., Severin, B. and Dale, B. (2003). FIBEX-treated rice straw as a feed ingredient for lactating dairy cows. *Animal Feed Science and Technology*, 41-50.
- Xiao, Q., Chen, Y., Gao, Y., Xu, H., and Zhang, Y. (2010). Leaching of silica from vanadium-bearing steel slag in sodium hydroxide solution. *Hydrometallurgy*. 104(2):216-221.
- Xu, H., Wei, C., Li, C., Fan, G., Deng, Z., Zhou, X., and Qiu, S. (2012). Leaching of a complex sulfidic, silicate-containing zinc ore in sulfuric acid solution under oxygen pressure. *Separation and purification technology*. 85: 206-212.
- Yagi, S. and Kunii, D.(1955). Studies on combustion of carbon particles in fames and fuidized beds. *In: Fifth Symposium (International) on Combustion, Reinhold,* New York, pp. 231–244.
- Yamashita, Y., Shono, M., Sasaki, C. and Nakamura, Y. (2009). Alkaline peroxide pretreatment for efficient enzymatic saccharification of bamboo. *Carbohydrate Polymers*. 79:914-920
- Yao, R.S., Hu, H.-j., Deng, S.-s., Wang, H. and Zhu, H.-x. (2011). Structure and saccharification of rice straw pretreated with sulfur trioxide micro-thermal explosion collaborative dilutes alkali. *Bioresource Technology*. 102(10): 6340-6343.
- Yang, H.H., Chien, S.M., Chao, M.R. and Lin, C.C. (2005), Particle Size Distribution of Polycyclic Aromatic Hydrocarbons in Motorcycle Exhaust Emissions. J. *Hazardous Materials*. 125: 154-159.
- Yang, J., Cao, Y., Cai, Y. and Terada, F. (2010). Natural populations of lactic acid bacteria isolated from vegetable residues and silage fermentation. *Journal of Dairy Science*, *93*(7):3136-3145.
- Yamagishi, K., Kimura, T. and Watanabe, T. (2011). Treatment of rice straw with selected Cyathus stercoreus strains to improve enzymatic saccharification. *Bioresource Technology*, 102(13): 6937-6943.
- Yu, J., Zhang, J., He, J., Liu, Z. and Yu, Z.(2009) Combinations of mild physical or chemical pretreatment with biological pretreatment for enzymatic hydrolysis of rice hull. *Bioresource Technology*. 100:903–908.
- Zadrazil, F., and Puniya, A.K., (1995). Studies on the effect of particle size on solid-state fermentation of sugarcane bagasse into animal feed using white-rot fungi. *Bioresource Technology*. 54:85–87.

- Zahiroddini, H., Baah, J., Absalom, W. and McAllister, T. A. (2004). Effect of an inoculant and hydrolytic enzymes on fermentation and nutritive value of whole crop barley silage. *Animal Feed Science and Technology*. 117(3–4): 317-330.
- Zeglinski, J., Piotrowski, G. P. and Piekos, R. (2006). A study of interaction between hydrogen peroxide and silica gel by FTIR spectroscopy and quantum chemistry. *Journal of Molecular Structure*. 794:83-91.
- Zhang, Y. H. P. and Lynd, L. R. (2004a). Towards an aggregated understanding of enzymatic hydrolysis of cellulose: Noncomplexed cellulase systems. *Biotechnology and Bioengineering*. 88:797–824.
- Zhao, X., Morikawa, Y., Qi, F., Zeng, J. and Liu (2014). A novel kinetic model for polysaccharide dissolution during atmospheric acetic acid pretreatment of sugarcane bagasse. *Bioresource Technology*. *151*:128-136.
- Zotov N, and Keppler H (2002) Silica speciation in aqueous fluids at high pressures and high temperatures. *Chemical Geological*. 184: 71 –82