



Faculty of Resource Science and Technology

**PREPARATION AND CHARACTERIZATION OF CELLULOSE NANOPARTICLES
AND NANOCOMPOSITE FILMS DERIVED FROM PRINTED PAPER WASTES**

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Declaration

I hereby declare that no portion of this dissertation has been submitted in support of an application for another degree of qualification of this or any other university or institution of higher learning.

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List of Abbreviations

Chemical Reagents

CH₃COOH: Acetic acid

CH₄N₂S: Thiourea

HCl: Hydrogen chloride

H₂NCONH₂: Urea

H₂O₂: Hydrogen peroxide

NaOH: Sodium hydroxide

NTU: Sodium hydroxide/ Thiourea/ Urea

KBr: potassium bromide powder

Whatman CF11: Whatman CF11 Fibrous Cellulose Powder

Symbols

cm: Centimeter

°C: Degree Celsius

g: Gram

kV: Kilovolt

mL: Millimeter

rpm: Revolution per minutes

v/v: Volumer per volume

wt%: Weight percentage

w/v %: Weight per volume

Instruments

FTIR: Fourier transformed infrared spectroscopy

SEM: Scanning Electron Microscope

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Preparation and Characterization of Cellulose Nanoparticles and Nanocomposite Films Derived from Printed Paper Wastes

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Abstract

The increasing amount of paper wastes generated around the world has caused disposal problems to our environment. Paper wastes are one of major cellulosic waste materials which include printed office papers, newspapers, magazines and books. In this study, cellulose was extracted from printed paper waste and then converted into cellulose nanoparticles and nanocomposite films. The paper wastes underwent pretreatment, dissolution and regeneration processes under controlled conditions. The nanoprecipitation technique was used to regenerate cellulose nanoparticles from dissolved cellulose solution. Particle sizes of cellulose nanoparticles were controlled by varying parameters such as cellulose concentration and addition of surfactant. The sago starch and cellulose nanoparticles were used to form green nanocomposite film. Both cellulose nanoparticles and nanocomposite films prepared from printed paper wastes were characterized by SEM and FTIR.

Keywords: paper wastes, cellulose nanoparticles, nanoprecipitation, green nanocomposite film

Abstrak

Jumlah sisa kertas yang dihasilkan di seluruh dunia semakin meningkat telah menyebabkan masalah pelupusan di alam sekitar kita. Sisa kertas adalah salah satu bahan-bahan buangan utama cellulosic termasuk kertas pejabat bercetak, akhbar, majalah dan buku-buku. Dalam kajian ini, selulosa telah diasingkan daripada sisa kertas bercetak dan kemudian menjadi kepada nanopartikel selulosa dan filem komposit nano. Bahan buangan kertas melalui rawatan awal, pembubaran dan pertumbuhan semula proses di bawah keadaan terkawal. Teknik pemendakan telah digunakan untuk menjana semula nanopartikel selulosa daripada larutan selulosa. Pelbagai parameter seperti kepekatan selulosa dan penambahan surfaktan telah digunakan untuk mengawal zarah saiz nanopartikel selulosa. Kanji sago dan nanopartikel selulosa telah digunakan untuk membentuk filem komposit nano hijau. Kedua-dua nanopartikel selulosa dan filem komposit nano yang diperolehi daripada sisa kertas bercetak telah dianalisis melalui SEM and FTIR.

Kata kunci: sisa kertas, nanopartikel selulosa, teknik pemendakan, filem komposit nano

1.0 Introduction

Globally, it is estimated that about 250 million tons of municipal solid waste (MSW) has been generated in 2010 and the largest portion of this disposed waste are cellulosic materials such as printed paper, paperboard, magazines, newspaper and etc. (Environmental Protection Agency, 2012). The improper handling of paper wastes has caused waste disposal problems. Landfill is the most common and cost effective disposal method but it can result in periodic fires, pollution of water supplies and possible spread of diseases. Alternative to landfills, incineration has also been used to dispose paper waste, but it is much more expensive. According to Clifford (1974), a new incineration facility could increase New York City's disposal costs by over 100%. Besides, both incineration and landfill disposal methods will cause environment problems due to production of greenhouse gases such as methane, carbon monoxide, carbon dioxide and nitro oxide during the disposal processes. Although recycling is a better way to deal with paper wastes, however not all paper and paper products can be recycled, and not everything that is recyclable is being recycled (Clifford, 1974). As a result, recycling can end up using more energy resources than paper made with new paper pulp since it requires labor and resources for collecting, sorting, transporting, de-inking, and milling all of which are very expensive processes. Due to the expensive cost of both monetary and social of waste disposal many would seek all possible means of reducing the volume of waste and therefore its disposal costs.

Using the paper waste as the raw material for other applications may not be the only answer to our garbage problems, but it is at least a partial answer. Paper wastes are reusable and recyclable materials which contain a myriad of organic and inorganic compounds. The organic

part consists of cellulose, hemi-cellulose, lignin and/or various compounds of lignin and constitute up to 70-100% of paper waste (Harry, 2010). The cellulose in paper wastes can be isolated through different mechanical and chemical processes. Cellulose is a polysaccharides that are consisting of (1,4)- β -linkage glucose units. It is a stable component due to presence of strong intra- and inter- hydrogen bonds. Cellulose contains nano-fibrillar structure which can self-assemble into well-defined pattern at multiples scales ranging from nano-scale to macro-scale (Chong, 2010).

In past 30 years, cellulose nanoparticles and nanocomposite has gained great attention of scientist because of their special properties such as high strength and stiffness combined with low weight, biodegradability and renewability. Besides, cellulose nanoparticles possess potential application in catalysis, molecular electronics, energy conversion and storage and as controlled drug carriers. Many researchers had been reported that cellulose nanoparticles can significantly improve physical, chemically and tribiological properties of different bulk materials (Dufresne, 2010; Hubbe *et al.*, 2008).

In this study, cellulose nanoparticles and nanocomposite films were prepared using environmental friendly and cost effective method by using printed paper waste as the raw material. Printed Paper wastes were pretreated with chemicals and mechanical processes such as acetic pulping and floatation de-inking. The pretreated printed paper wastes were dissolved in NaOH/ thiourea/urea (NTU) solvent system. The cellulose was regenerated into nano-scaled particles using the nanoprecipitation method by adding cellulose solution into excess absolute ethanol. Different parameters such as ratio of cellulose solution to non-solvent, concentration of cellulose solution and addition of surfactant (Tween 80) were used to determine particle

size and morphology. The regenerated cellulose nanoparticles were used to form green nanocomposite film with sago starch as matrix. The physical and chemical properties of the cellulose nanoparticles and nanocomposite films are investigated by Scanning Electron Microscope (SEM), and Fourier Transformed Infrared Spectroscopy (FTIR).

1.1. Objectives

The objectives of the study are:

- i) Preparation of cellulose nanoparticles of various sizes from printed paper wastes by using nanoprecipitation techniques.
- ii) Preparation of green starch/cellulose nanocomposite films from the regenerated cellulose nanoparticles.
- iii) Characterization of cellulose nanoparticles and nanocomposite films using Scanning Electron Microscope (SEM), and Fourier Transform Infrared Spectroscopy (FTIR).

2.0 Literature Reviews

2.1. Pulping Process

Cellulose is the most abundant and available renewable polysaccharides resources in today worldwide. It can be isolated directly from the different plant species or cellulosic materials such as paper wastes, facial cotton and tissue paper. The first treatment of the extraction process is pulping.

The main purpose of pulping is to separate wood fibers and also remove the lignin present in the in fibers to produce pulps. There are three types of processes that can be used to produce pulps which are chemicals, mechanical and combination of processes (Wegener, 1993). Sulfate pulping (Kraft pulping) and sulfite pulping are two types of chemical pulping which were commonly been used to create pulp. The following are the three steps involved in the chemical pulping (Brady *et al.*, 1998).

1. Digestion process whereby the fibers are cooked to dissolve the lignin.
2. Washing process to separating the formed pulp from black liquor.
3. Chemical recovery process. Sodium sulfide (Na_2S) and sodium carbonate (Na_2CO_3) are recovered from the black liquor for reuse.

Kraft pulping process was developed in Germany in 1879 and was first applied to a Swedish mill in 1885 (Brady *et al.*, 1998). The paper produced by using Kraft pulping process has higher strength than other paper previously made but the colour of paper created was dark

brown. Therefore, bleaching process is needed to produce much lighter paper (Brady *et al.*, 1998).

Sulfite pulping had been developed in 1867 (Brady *et al.*, 1998). The colour of pulp produced from sulfite pulping process is much lighter in comparison to the pulp from Kraft pulping (Brady *et al.*, 1998). Nevertheless, this type of pulping yields lower pulp strength properties and also produces low percentages of pulp when using hardwood as the raw materials. Most steps of sulfite pulping are similar to Kraft pulping. The only difference is the solvents added during the delignification process. In digestion process, sulfite pulping process involves using a mixture of sulfurous acid and bisulfate ion in the form of calcium, magnesium, sodium, or ammonium bisulfate as solvent while Kraft pulping process uses a mixture of sodium hydroxide and sodium sulfide (Brady *et al.*, 1998).

Although both Kraft pulping and sulfite pulping processes are effective in producing pulp, however they still cause pollution and odor problems due to chemicals that have been used to dissolve the lignin present in wood fibers. Therefore, alternative environment friendly ways to create pulp such as the Organocell process, Alkaline sulfite anthraquinone methanol (ASAM) pulping and Acetosolv process were developed by reducing the use of chemicals. Organocell process is the pulping process that uses different organic solvents such as methanol, ethanol, acetic acid, soda-lime and ethanol-alkali instead of sulfur compound to separate lignocellulosic materials as pulp, lignin and solvated wood sugars (Sarkanen, 1990). Therefore, sulfur-free pulping was achieved and the pollution problems were also reduced (Wegener, 1993). Besides, the strength properties of pulp produced by this method are between those of

sulfite and sulfate pulp. However, a feasible organosolv pulping process with cost effective delignification has not been developed until now in the industry (Hergert, 1998).

ASAM pulping is another alternative method to replace the conventional pulping process. This method was adapted from sulfite pulping. ASAM pulping process consists of three main sections which are digestion and brown stock washing, screening and four-stage bleaching, evaporation and methanol rectification (Tulenheimo, 1997). The advantage of the ASAM pulping compared to Kraft pulping is that it is easier and more effective bleach ability, resulting in a good brightness pulp (Weneger, 1993).

In 1992, another new pulping process, Acetosolv had also been established. (Weneger, 1993). The pulping was principally carried out with mixture of acetic acid followed by oxidizing agent bleaching in acetic medium (Pang *et al.*, 2011; Weneger, 1993). The common oxidizing that been used was hydrogen peroxide (H_2O_2). The photolysis of hydrogen peroxide with the formation of hydroxyl radicals, peroxyradicals and other active oxygen species can cleave any in the carbohydrate chains lignin, hemicelluloses and also amorphous part of cellulose (Glady *et al.*, 2001). The destruction of glycosidic linkage has results the dispersion of the cellulose fibers from each other.

In addition, the efficiency of this pulping had improved by adding tin oxide (TiO_2) as catalyst and the reaction was under the UV- radiation condition (Kuznetsov *et al.*, 2009). As reported by Kuznetsov *et al.* (2009), the combination action of UV-irradiation and TiO_2 catalyst allow producing of chemically pure cellulose containing no residual lignin. The promoting action of UV-irradiation on wood pulping process was due to UV-irradiation had activated the photo

excited groups of lignin leading to easy react with active oxygen species (Kuznetsov *et al.*, 2009; Lanzalunga *et al.*, 2000). Besides, the UV-irradiation had increased the photolysis of hydrogen peroxide. The same can make the TiO₂ catalyst sunder UV-irradiation. However, Kuznetsov *et al.* (2009) had reported that the UV pretreatment reduces the yield of cellulosic product up to 35.7 wt%.

2.2. Deinking Process

De-inking process was an addition process need to be conducted in isolation of cellulose fibers from paper wastes. This process was very essential since it allows the resulting material to have suitable properties for reuse (Costa & Rubio, 2005). There were many methods that had been developed for de-inking. For conventional deinking, a lot of chemicals need to be used such as sodium hydroxide, hydrogen peroxide, chelating agents, sodium silicates and other collector chemicals (Venugopal, 1998). Therefore, quantity and types of chemicals used were the main role in controlling the efficiency of the deinking process. For example, sodium hydroxide was used to control the pH of the aqueous medium to alkaline and also softens and swells the pulp fibers. As reported by Venugopal (1998), the alkalinity of aqueous medium in the deinking process should be controlled at pH 10.2 so that brightness of the pulp can be maintained. The pH of alkalinity aqueous medium above 10.2, the brightness of the pulp was decreased due to the formation of chromophores in lignin. Hydrogen peroxide is a very important reagent in the bleaching process because it produces perhydroxyl ions which can reduce alkali darkening that occurs due to use of sodium hydroxide, by maintaining the brightness of the pulp (Venugopal, 1998). However, efficiency of hydrogen peroxide is easily affected by the presence of heavy metal ions in inks and enzymes because they decompose the hydrogen peroxide. In order to curb this problem, chelating agents and sodium silicates were

used to form soluble complex with metal ions which can easily be removed away by washing the pulp (Venugopal, 1998).

Floataction de-inking method is the most common practice used to remove ink from paper waste. There are three main processes in the floatation deinking, namely, detachment of the ink particles from the fibers, adhesion of the ink particles onto air bubble surface and removal of froth and ink particles from flotation cells (Zhao *et al.*, 2004). Surfactants play a key role in this process. As reported by Zhao *et al.* (2004), the utilization of surfactants are for removing ink particles from the fibers, stabilizing liberated particles, aggregating dispersed particles and/or modifying the surface properties of released ink particles, and enhance the overall ink removal of a flotation line. Surfactants that are normally used in the treatment are fatty acid soaps or nonionic surfactants. In 2005, Costa and Rubio had conducted research on the influences of calcium soap and surface- active substances on the floatation deinking process. These experiments were carried out by using Ca(oleate)_2 , CaCl_2 , sodium oleate, sodium dodecyl sulfate (SDS) and sodium benzene dodecyl sulfate (SBDS). This study had shown that, the use of Ca(oleate)_2 combined with SDS will remove the ink more effectively than Ca(oleate)_2 by itself (Costa & Rubio, 2005). The paper pulp recovery rate was lower in the tests in which SDS and SBDS were used without Ca(oleate)_2 (Costa & Rubio, 2005).

In 2004, Venditti had reported a simple floatation deinking experiment which can easily be conducted in laboratory and this method is also cost effective and environmentally friendly because the only chemical used is detergent to form foam. In the process, fine air bubbles were sparged into the beaker which containing paper pulps and the hydrophobic contaminants like ink particles preferentially attach to the bubble-water interfaces and float to the surface

(Venditti, 2004). The foam rich with contaminant then is removed resulting in the separation.

Figure 1 is the schematic diagram of the floatation de-inking process.

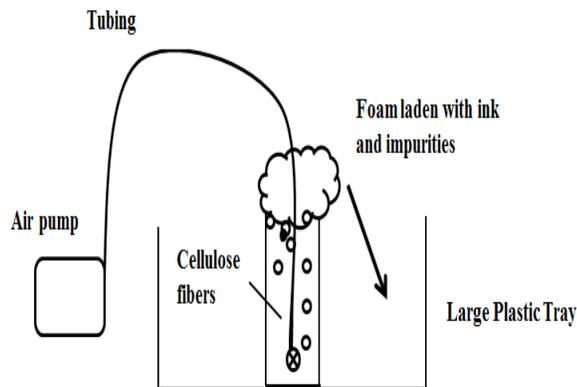


Figure 1: Schematic diagram of the floatation de-inking process (Venditti, 2004).

Besides, another method for deinking is bio-deinking. Bio-deinking was known as enzymatic deinking which uses reagents of celluloses and hemicelluloses to dislodge ink particles from the fiber surface (Heitmann *et al.*, 1992). The enzymes used in the treatment include lipases, amylases, xylanases and cellulases. After the treatment, the flotation process was conducted to remove the released ink particles by using calcium chloride only, without the use of conventional alkaline deinking chemicals (Heitmann *et al.*, 1992).

2.3. Dissolution of Cellulose Fibers

Cellulose has strong intra- and inter- molecular hydrogen bonding which make it very hard to dissolve in any organic and inorganic solvents (Kihlman, 2012). In order to dissolve cellulose fibers, the solvent molecules must be able to penetrate into cellulose molecules and disrupt the crystallite in cellulose derivatives and also the hydrogen bonding (Swatloski *et al.*, 2002).

Cuprammonium hydroxide solvent and viscose process were the most traditional solvent

system developed to dissolve the cellulose fibers. However, these two solvent systems had causes negative effect to environment due to the huge amount of hazardous chemicals produced.

Aqueous solutions of sodium hydroxide (NaOH) are the popular cellulose solvents in today due to the ease of solution preparation, cost-effective and more environmental friendly. In 1998, Laszkiewicz had studied the solubility of bacterial cellulose and its structural properties. The author had also reported that the addition of 1 wt% urea to 8.5 wt% NaOH at -5 °C improves the solubility of bacterial cellulose with an initial degree polymerization (DP) of 680. The percentages of dissolved cellulose are 48.6% with 1wt% urea and 17.8% without urea.

After some years later, a research group in China had proven that cellulose can be effectively dissolve in NaOH with urea (Wang *et al.*, 2007, 2008; Zhao *et al.*, 2004; Zhou *et al.*, 2002) or thiourea (Zhang *et al.*, 2008, 2010) and that both added reagents can be removed efficiently from the cellulose during the coagulation and washing steps. Zhou and Zhang (2000) investigated the influence of the NaOH/urea solvent composition on cotton linter dissolution. They concluded that the optimal NaOH/urea/water ratios for dissolution of cellulose were 6 wt%/4 wt%/90 wt% and 8 wt%/2 wt%/90 wt%, but that the solubility of cellulose decreases when its degree of polymerization (DP) increases.

In recent years, Zhang *et al.* had developed a new alkaline complex aqueous solvent that consisted of sodium hydroxide (NaOH), thiourea and urea (NTU) to dissolve cellulose fibers. The reported optimal composition of NTU to be effectively dissolve the cellulose fibers were NaOH (8 wt%), thiourea (6.5 wt%) and urea (8 wt%) and NTU solvent pre-cooled at -10 °C.

This optimal condition can readily produce stable cellulose solutions at relatively high concentrations. In the system, NTU solution breaks down the intra- and inter-molecular hydrogen bonding of cellulose and prevents cellulose molecules from approaching toward each other, leading to the dissolution of cellulose. Since the dissolution process was an exothermic process, increasing of the temperature will decrease the strength of the solvent network structure and interactions between cellulose and solvent lead to incomplete dissolution (Zhang *et al.*, 2010). In addition, Zhang *et al.* (2010) also shown that, gelation formed in the semi-dilute entangled solutions and the gelling temperature lowered with addition of cellulose concentration in the solution. Besides, this solvent system do not degrade cellulose even after storage times of up to one month which reported by Zhang *et al.* (2010).

Egal *et al.*, (2008) had studied the dissolution of microcrystalline cellulose in hydroxide-urea aqueous solutions. Their research was focused on mechanisms of this dissolution and the interactions between the components and the binary phase diagram of urea/water. Egal *et al.* (2008) had shown that urea was not directly interacting with NaOH or with cellulose based on the binary phase diagram produced by the DSC technique. This implies that the chemical reaction in cellulose/NaOH/water solution does not make any new compounds with NaOH or cellulose (Egal *et al.*, 2008). The function of urea is to trap the free water that is present in solution, preventing interaction of the cellulose chains to associate via hydrogen bond formation (Egal *et al.*, 2008). The authors are also expected thiourea has the function as the urea (Zhang *et al.*, 2010; Egal *et al.*, 2008).

2.4. Regeneration of Cellulose

The viscose process was the earliest method used to regenerate cellulose from its solvent system (Chong, 2010). The cellulose regenerated was called viscose rayon. This process was conducted by treating the cellulose with alkali and carbon disulfide to yield viscose (Chong, 2010). The main drawback of the viscose process is its negative impacts on the environment due to the use of carbon disulfide.

Besides, cellulose can be regenerated by adding of excess non-solvent. The non-solvent usually been used were acetone, alcohol and water. Li *et al.* (2011) had successfully regenerated the cellulose by added water to the cellulose/NaOH/urea solution at temperature 25 °C to 45 °C. “The inclusion complex associated with cellulose, NaOH and urea hydrates in the cellulose solution were broken by adding water (non-solvent), leading to the self-association of cellulose to regenerate through rearrangement of the hydrogen bonds” (Li *et al.*, 2011). The condition of regeneration process can be control to produce cellulose nanoparticles. This process is known as nanoprecipitation technique. Nanoprecipitation is a facile, mild and low energy input process for preparation of polymeric nanoparticles. In this process, the successive addition of sample solution into a non-solvent leads to sample precipitation on the nano-scale. Figure 2 is the schematic diagram of formation of nanoparticles by adding of non-solvent.

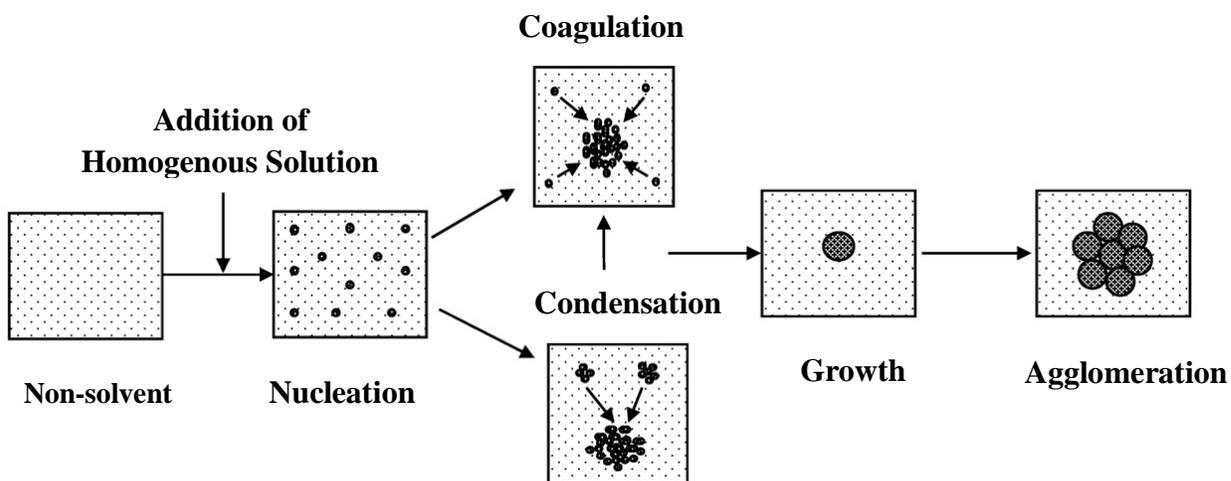


Figure 2: Schematic of nanoprecipitation process (Alpana & Sameer, 2012).

Bilati *et al.* (2005) had reported using alcohol as non-solvent to prepare polymeric nanoparticles. The coauthor had shown that the final sizes of particles increased in the sequence: methanol < ethanol < propanol < butanol. The particles sizes was depend on the rate of diffusion, the higher the diffusion rate, the smaller the sizes of formed nanoparticles.

In 2011, Chin *et al.* had successful prepares nanoparticles from native sago starch by a simple nanoprecipitation. The non- solvent been used is absolute ethanol and the sizes of particles formed were approximately 300 nm to 400 nm. Besides, the particles sizes are also controlled by using non-ionic surfactant (Tween 80) and anionic surfactant (hexadecyl (cetyl) trimethylammonium bromide (CTAB)). The mean particle sizes are reduces to 150 nm to 200 nm and 250 nm to 300 nm in present of Tween 80 and CTAB respectively (Chin *et al.*, 2011).

2.5. Application of Cellulosic Products from Paper Wastes

Paper waste is made up of wood fibers which containing abundant of the cellulose. Due to this, people have tried to turn it into more useful product. Recycling is the most common method used by people to reuse the waste paper. Many products had been created by using cellulose isolated from the waste paper such as cellulose insulation, bio-fuel, ceramics and cement and so on. Besides, some scientists had also started using waste paper as a raw material in their research to exploit its potential applications in different fields. Waste paper is a good cellulosic material for producing environment friendly fuel since cellulose can be converted enzymatically to glucose and subsequently fermented to ethanol (Wu & Ju, 1998; Wood *et al.*, 1997; Scott *et al.*, 1994). As reported by Lark *at el.* (1997), a least 72% of cellulose in the recycle paper sludge was converted to ethanol by using cellulose and yeast, *Kluveromyces Marxianus*. The advantages of using recycled paper sludge to produce ethanol not only can reduce the disposal cost and at the same time can produce a bio- fuel. Dubey *at el.* (2012) had reported the production of bio-ethanol from paper wastes through acid pretreated hydrolyzate with xylose fermenting *Pichiastipitis*. “Fermentation of acid hydrolyze of wastepaper with *Pichiastipitis* under optimum condition resulted in ethanol production 3.73 ± 0.16 g/l with $77.54 \pm 4.47\%$ of fermentation efficiency” (Dubey *et al.*, 2012).

In 2011, Pang *et al.* had developed nanostructured ceramics and nanocomposites from cellulosic waste materials. They had successfully converting the cellulosic material, waste paper into nanostructured SiO₂ ceramics and carbon/SiO₂ nanocomposites by submering them with silica sol and then underwent calcinations process under at 550 °C in air and nitrogen (Pang *et al.*, 2011). “The nanostructured ceramics and nanocomposite materials could be