SYNTHESIS AND CHARACTERISTICS OF MAGNETIC HYDROGELS PREPARED FROM SAWDUST AND ITS POTENTIAL APPLICATION IN HYDROGEN PRODUCTION

NURUL AINA BINTI IDRUS

UNIVERSITI SAINS MALAYSIA

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by

NURUL AINA BINTI IDRUS

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LIST OF ABBREVIATIONS

BET	Brunauer-Emmett-Teller
CaH_2	Calcium Hydride
CO_2	Carbon Dioxide
Fe_3O_4	Iron Oxide
$FeCl_3$	Iron Chloride
FTIR	Fourier Transform Infrared Spectroscopy
HEMA	2-Hydroxyethyl Methacrylate
K_2CO_3	Potassium Carbonate
LiH	Lithium Hydride
MA	Maleic Acid
MF	Magnetic Force
MgH_2	Magnesium Hydride
MH	Magnetic Hydrogel
MSW	Municipal Solid Waste
$NaBH_4$	Sodium Borohydride
NAOH	Sodium Hydroxide
NH_4OH	Ammonium Hydroxide
p(AMPS)	Poly(2-Acrylamido-2-Methylpropanesulfonic Acid)
rpm	Revolution per minute
SD-MH	Sawdust-Magnetic Hydrogel
WSAC	Wood Sawdust Activated Carbon

SINTESIS DAN CIRI-CIRI HIDROGEL BERMAGNET YANG DISEDIAKAN DARI SERBUK KAYU DAN POTENSI APLIKASINYA DI DALAM PENGHASILAN HIDROGEN

ABSTRAK

Sebagai pembawa tenaga yang bersih, hidrogen dijangkakan sebagai salah satu sumber tenaga utama menjelang abad ke-21 dan juga sebagai salah satu pilihan sumber tenaga alternatif bagi menggantikan bahan api fosil. Tujuan utama kajian ini adalah untuk mencipta satu sistem pemangkin yg boleh terlaksana untuk menjana pengeluaran hidrogen dari hidrolisis yang dimangkinkan oleh natrium borohidrit. Serbuk kayu hidrogel bermagnet telah disediakan dari prosedur sambung silang bersama serbuk kayu dan garam besi yang murah dan mesra alam. Serbuk kayu iaitu sisa selulosa yang disambung silang dengan garam besi untuk menjadi hidrogel bermagnet akan menjadi satu bahan alternatif baru untuk menghasilkan hidrogen. Sisa selulosa diklasifikasikan sebagai bahan penjerap murah kerana ia boleh didapati dari pelbagai sumber semula jadi. Di dalam kajian ini, jumlah pemangkin, kepekatan natrium hidroksida, dan kesan suhu ke atas aktiviti pemangkin kepada penghasilan hidrogen dari hidrolisis natrium borohidrit telah disiasat sepenuhnya. Kombinasi 2.5wt% natrium borohydride dan 15wt% natrium hidroksida didapati telah menghasilkan prestasi tertinggi untuk penghasilan hidrogen pada suhu 30°C dengan jumlah pemangkin paling sedikit iaitu sebanyak 0.2g. Pemangkin telah dicirikan dengan teknik-teknik Isotem Brunauer-Emmett-Teller (BET), Spektroskopi Fourier Mengubah Inframerah (FTIR) dan unsur analisis. Kajian BET menunjukkan kawasan permukaan hidrogel bermagnet iaitu $77.7311m^2$/g. Kajian FTIR pula dijalankan untuk memahami jenis-jenis kumpulan berfungsi di dalam serbuk kayu yang

bertanggungjawab untuk proses mengikat logam manakala kajian unsur analisis pula diadakan untuk mengkaji elemen komposisi di dalam pelbagai jenis serbuk kayu yang telah disediakan.

SYNTHESIS AND CHARACTERISTICS OF MAGNETIC HYDROGELS PREPARED FROM SAWDUST AND ITS POTENTIAL APPLICATION IN HYDROGEN PRODUCTION

ABSTRACTS

As a clean energy carrier, hydrogen is expected to be one of the main energy sources in the 21st century and one of the candidates for an alternative energy carrier to replace fossil fuels. The basic aim of this study is to develop a feasible a new catalyst system for the hydrogen generation by catalytic hydrolysis of sodium borohydride, $NaBH_4$. Sawdust-magnetic hydrogel (SD-MH) was prepared by a crosslinking procedure with cheap and environmentally friendly sawdust and iron salts. Sawdust which is a cellulose waste crosslinked with iron salts to form magnetic hydrogel will become the new alternative for hydrogen production. Cellulosic material is classified as cheap adsorbents because it can be obtained from various natural sources. In this study, catalyst amount, sodium hydroxide (NaOH) concentration, and the effects of temperature on the catalytic activity toward hydrogen production from hydrolysis of $NaBH_4$ are completely investigated. It was found that the combination of 2.5wt% $NaBH_4$ and 15wt% NaOH yields the highest performance for the hydrogen generation at 30°C with the lowest catalyst amount of 0.2g. The catalysts were characterized by Brunauer-Emmett-Teller Isotherm (BET), Fourier Transform Infrared Spectroscopy (FTIR) and Elemental Analysis techniques. BET study shows the surface area of magnetic hydrogel of 77.7311 m²/g. FTIR studies were carried out to understand the type of functional groups in sawdust responsible for the metal binding process while elemental analysis is done to study the composition elements in the prepared sawdust of different types.

CHAPTER 1: INTRODUCTION

1.1   Research Background

The world has limitation to the supply of fossil fuel nowadays, thus the development of alternative and clean renewable energy carriers is most important. Hydrogen is expected to be one of the main energy sources in the 21st century and the most abundant element in the universe. However, it has to be produced from other sources as it does not exist by itself on Earth. Hydrogen is produced by various energy sources such as natural gas, coal, water and renewable energy sources. Hydrogen can be converted again into useful energy using fuel cells (Sahin et al., 2016). Researchers have focused their attention on hydrogen production from chemical hydrides such as CaH_2, LiH, $NaBH_4$, MgH_2, $LiAlH_4$, and NH_3BH_3. $NaBH_4$ is the most widely used of these hydrogen storage materials due to its advantages such as nontoxic properties, high hydrogen storage capacity (10.8%), non-flammability of the basic aqueous solution, stability in air and easily controlled hydrogen generation rate. In the presence of the catalyst, the hydrolysis basic aqueous sodium borohydride solution is exothermic and yields two fold more hydrogen than its content (Sahiner et al., 2011). Şahin et al. (2010) stated that to generate hydrogen from alkaline $NaBH_4$ solution, a suitable catalyst is needed to promote the hydrolysis. Extensive study to different catalysts such as ruthenium (Ru), cobalt (Co) supported catalyst, nickel (Ni) based catalyst, Co-Ni catalyst, Ni-B catalyst, Ni-CoB catalyst, copper(Cu)-Co catalyst, rhodium (Rh), platinum (Pt), PtRu, Co-B/Pd, Pt-Ru, Pt-Pd alloys is done to find the suitable catalyst. However, due to the high price of noble metal catalysts, there is needed to develop alternative catalysts based on cheaper transition metals.

Hydrogel referred to as intelligent materials, due to their responsiveness to small changes in the environment and water-swollen crosslinked networks of the hydrophilic polymer. They have hydrophilic groups in their backbones, thus they can absorb a large amount of water and swell. The hydrogel can be modified with new functional groups or prepared as composites to increase their metal absorption capacity and their versatility for practical usage (Ozay et al., 2010). Thus, the hydrogel can be the best catalyst for hydrogen generation. According to Sahiner et al. (2011), hydrogel has a wide range of applications in various areas including medical fields, environmental fields, sensors, separation and purification processes. The magnetic hydrogel has also been produced by filling hydrogel with magnetic particles (Toth et al., 2015). Magnetic separation has become a promising method for environmental purification as it produces no contamination and it is easily separated from the medium under applied magnetic field. Hydrogel with magnetic properties has become a new class of intelligent materials which attract interest as a catalyst in hydrogen generation. As hydrogel as extremely porous and have a three-dimensional network structure, they can absorb species in their network as well as on their surfaces (Ozay et al., 2010).

Cellulose waste crosslinked to magnetic hydrogel will become a new alternative for hydrogen production. Recently, there are a few research of cellulose waste adsorption onto magnetic hydrogel such as chitosan (Shen et al., 2011), rice and oat husks (Oliviera et al., 2016), tea residue (Liu and Huang, 2016), bamboo shoot (Liu et al., 2016), etc. It is well known that cellulosic materials can be obtained from various natural sources and can be employed as cheap adsorbents. In general, chemically modified cellulose exhibits higher adsorption capacities for various aquatic pollutants than their unmodified forms. Cellulose is argued to be the most

abundant polymer in nature and constitutes the main component of plant fibers, giving the plant rigidity. Cellulose is a biopolymer raw material and has served mankind in numerous applications as a construction material, mainly in the form of intact wood and textile fibers such as cotton or flax, or in the form of paper and board. Cellulose can be derived from a variety of sources, such as woods, annual plants, microbes, and animals. These include seed fiber (cotton), wood fibers (hardwoods and softwoods), bast fibers (flax, hemp, jute, ramie), grasses (bagasse, bamboo), algae (Valonica ventricosa), and bacteria (Acetobacter xylinum). In addition to cellulose, these materials also contain hemicelluloses and a small amount of lignin. Wood and cotton are the raw materials for the commercial production of cellulose. It is well known that cellulosic-based materials can be obtained and employed as cheap adsorbents, and their performance to remove heavy metal ions can be affected by chemical treatment. In general, chemically modified cellulose materials exhibit higher adsorption capacities than unmodified forms (Hokkanen et al., 2016).

1.2   Problem Statement

Hydrogen can be produced from a variety of abundant precursors, such as natural gas, coal, water and renewable energy sources. However, it does not exist by itself on earth and the supply of fossil fuels is limited. Researchers have found that sodium borohydride ($NaBH_4$) had been used as the hydrogen storage materials due to its safe property and economical cost compared with other chemical hydrides. Unfortunately, the $NaBH_4$ solution is unstable and usually hydrolyzed to release hydrogen spontaneously even without catalysts. Researchers are done to find the suitable catalysts. The cost and availability of catalysts in the process hydrogen

generation from hydrolysis of $NaBH_4$ with various catalysts are predominantly parameters as there are many engineering problems, such as high cost, low catalyst durability caused by solubility limitations of sodium by-products, borohydride and sodium metaborate ($NaBO_2$) in an aqueous solution. Noble metal-based catalysts using Ruthenium (Ru) and Platinum (Pt) have been reported to promote high catalytic activity for the hydrolysis of $NaBH_4$, but there are many limitations in real application due to high cost and short lifetime. Thus, they cannot be mass-produced for industrial application although noble metal catalysts were proving higher effective for the hydrolysis of $NaBH_4$. Hydrogel, which is the intelligent materials are being utilized as a catalyst but however has the aggregation problems, which causes a reduction in catalytic activation of metal particles. The magnetic hydrogel is introduced as magnetic filling hydrogel to be easier collected by magnetic separation. Many variables towards magnetic hydrogel will be done to study the catalytic performance of magnetic hydrogel such as the amount of catalyst, the reaction temperature and NaOH concentration in the hydrolysis of $NaBH_4$. For example, in the study by Sahin et al. (2016), the amount of magnetic hydrogel used as a catalyst in hydrogen production produced different results due to varies of catalytic performance of magnetic hydrogel. Besides that, sawdust that is being thrown at the sawmill factory will be wasted. Thus, sawdust can be used as an alternative that transforms the waste into raw materials for the synthesis of the magnetic hydrogel to produce hydrogen.

1.3　Research Objectives

The objectives of this research are:

1. To synthesize and develop magnetic hydrogel from sawdust by crosslinking method.
2. To investigate the potential use of sawdust magnetic hydrogel and to study the effect of operating parameters (amount of catalyst, sodium hydroxide (NaOH) concentration, temperature of reaction) in hydrogen production.
3. To characterize the prepared sawdust-magnetic hydrogel using Elemental Analysis, Fourier Transform Infrared Spectroscopy (FTIR) and Brunauer–Emmett–Teller (BET) analysis.

1.4　Scope of Study

The scope of study for this project is divided into three phases. First, synthesis of magnetic hydrogel from raw materials which is sawdust. It used the cross-linking method in order to produce sawdust-magnetic hydrogel (SD-MH). The pore size and surface area are observed using BET. Meanwhile, elemental analysis is used to study the elemental composition in the magnetic hydrogel. Next, to determine the functional groups of the compound in the magnetic hydrogel, FTIR method is used.

Second, a study on the performance of hydrolysis of $NaBH_4$ is carried out by measuring the volume of hydrogen produced versus the time taken. After synthesizing SD-MH with different amount of sawdust, they are tested with hydrolysis of sodium borohydride as to find out the best catalyst to catalyze the hydrolysis of sodium borohydride.

Third, a study of different variable towards hydrolysis of sodium borohydride. Sodium borohydride is first hydrolyzed with different amount of catalyst. After that, to compare the difference in sodium hydroxide concentration with the volume of hydrogen production. Lastly, the temperature of the solution is varied to study the effect of temperature on hydrolysis of sodium borohydride. In each test, the volume of hydrogen produced is recorded for one hour with 5 minutes interval.

1.5   Organization of thesis

The following are the contents for each chapter in this study:

Chapter 1 introduces the research background of hydrogen production, magnetic hydrogel and cellulose waste together with problem statement, research objectives and organization of thesis.

Chapter 2 discusses the literature review of this study which includes hydrogel, magnetic hydrogel, cellulose waste, sawdust and hydrogen production

Chapter 3 covers the materials and details of methodology. It discusses on the description of equipment and materials used, pretreatment of the sawdust, synthesis of sawdust, analysis of sodium borohydride, factors affecting hydrogen production and characterization of prepared sawdust using elemental analysis, FTIR and BET analysis.

Chapter 4 refers to the experimental results and discussions of the data obtained. Further elaboration on the factors affecting hydrogen production and characterization results of the prepared sawdust-magnetic hydrogel.

Chapter 5 concludes all the findings obtained in this study. Recommendations are also included as well.

CHAPTER 2: LITERATURE REVIEW

2.1   Hydrogel

2.1.1   History of Hydrogel

In 1936, DuPont's scientists published a paper on the recently synthesized methacrylic polymers is where the history of hydrogel started. In this paper, they mentioned about poly (2-hydroxyethyl methacrylate) (polyHEMA). polyHEMA was briefly described as a hard, brittle and glassy polymer, and was clearly not considered of importance. After that research, until 1960, polyHEMA was essentially forgotten when Wichterle and Lim described the polymerization of HEMA and crosslinking agents in the presence of water and other solvents. They obtained soft, water swollen, elastic and clear gel, instead of brittle polymers. The modern field of the biomedical hydrogel, as we know them today is led by this innovation. The number of hydrogel formulations steadily grew over the years after that (Ahmed et al., 2013).

2.1.2   Properties of Hydrogel

Over the years, researchers have defined hydrogel in many different ways. Hydrogel according to Ahmed et al. (2013) is polymer networks extensively swollen with water. Hydrogel is referred to hydrophilic gels which are networks of polymer chains that are sometimes found in colloidal gels where water is the dispersion medium. Swelling experiments were carried out by Ahmed et al. (2012) with a view of evaluation of the swelling capacity of the prepared hydrogel in distilled water and at different pH values. Results of these experiments showed that the increase in weight of the swollen hydrogel is directly related to the duration of swelling. The free

network spaces between hydrogel networks functioned to accommodate and stabilize nanoparticles. Similar definition made by Ullah et al. (2015), hydrogel is a three-dimensional network of polymers which is made of natural or synthetic materials that are possessing a high degree of flexibility due to large water content. Under physiological conditions, they are able to retain a large amount of water or biological fluids and as they are characterized by a soft rubbery consistency similar to living tissues, making them an ideal substance for a variety of applications. Meanwhile, Shen et al. (2015) have defined hydrogel as a derivation from physically or chemically cross-linked polymers that produced three-dimensional network hydrophilic polymers. Hydrogel is sometimes referred to as intelligent materials or smart materials as it can exhibit significant volume changes in response to small changes in their environments. pH, temperature, electric field, solvent, ionic strength, and light are the example of the environmental conditions that can be received as stimuli (Ozay et al., 2010).

The stimuli-responsive hydrogel is called environmentally sensitive or smart hydrogel because it can respond to environmental stimuli and experience unexpected changes in their growth actions, network structure, mechanical strength and permeability (Peppas et al., 2000; Gil and Hudson, 2004). The ability to swell and shrink when the temperature changes in the surrounding fluid are the definition of temperature sensitive hydrogel, which means the swelling and deswelling behavior mostly depend on the surrounding temperature (Richter, 2010).

2.1.3 Characterization of Hydrogel

According to Ullah et al. (2015), hydrogel may be cationic, anionic or neutral, depending on the charges on the bound groups. One of the criterions for classification is the types of crosslinking agent that determined hydrogel can be physical or chemical. Hydrogel is also possible to divide into groups by their structure which is amorphous, semi-crystalline, crystalline and hydrocolloid aggregates. Figure 2.1 represents the classification of hydrogel based on their sources and properties, along with detailed classifications based on their response, example, physically, chemically and biochemically responsive hydrogel.
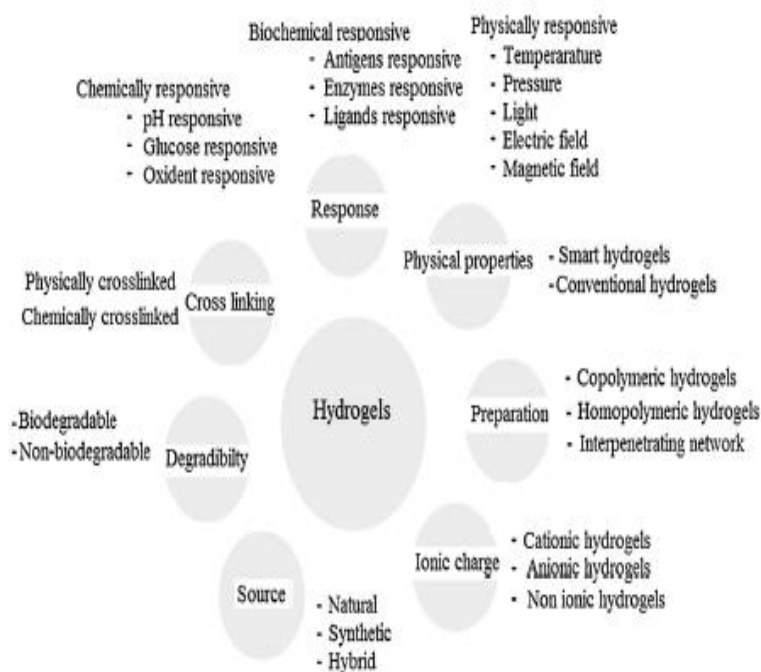
Figure 2.1: Characterization of hydrogel (Ullah et al., 2015)

The classification of hydrogel also depends on their physical properties, nature of swelling, method of preparation, origin, ionic charges, sources, the rate of biodegradation and observed nature of crosslinking. The nature of the crosslinking process is classified into physical gel that is normally achieved via physical processes

such as hydrophobic association, chain aggregation, crystallization, polymer chain complexion, and hydrogen bonding. On the other hand, a chemical process, such as chemical covalent crosslinking either simultaneously or post polymerization is utilized to prepare a chemical hydrogel. Physical hydrogel is reversible due to the conformational changes while chemical hydrogel is permanent and irreversible because of configurationally changes. Another category is the dual-network hydrogel, formed by the combination of physical and chemical crosslinked hydrogel via electrostatic interaction. It has recently been employed as it can overcome the disadvantages of solely using physical or chemical hydrogel with a high liquid uptake capacity over a wide range of pH and a higher sensitivity towards changes in the pH as compared to chemical hydrogel (Ullah et al., 2015).

2.1.4 Utilization of hydrogel

Hydrogel has incredible purposes in engineering, biology and pharmaceutical sciences with a momentous collection of resources. The hydrogel provides a platform for a range of applications including for microfluidic control, biomimetic, biosensor/bioactuator, bioseparation and artificial skin and muscles, due to the wonderful properties of the smart hydrogel, such as its reversible swelling/deswelling behaviour, high environmental sensitivity, high ionic conductivity, high permeability, surface properties, novel mechanical properties and sorption capacity (Ullah et al., 2015).

Hydrogel which find applications in medical implants (Park and Hoffman, 1990), prosthetic muscles or organs, robotic grippers, diagnostic devices to artificial muscles (Suzuki, 1989), stabilization of bone implants, intimal thickening in animals

and decreasing thrombosis (Hill-West et al., 1994) as it can copy the behaviour of human organs in response to change in environmental conditions such as pH, temperature, enzymes and electric field.

Other than that, in pharmaceutical industry, hydrogel plays a vital role as hydrogel is used as controlled drug delivery. It is able to load a wide variety of drugs into their structures and substantially protect them from physiological conditions, particularly those of the stomach where pH is low and enzyme concentrations are high or in other words, conditions under which many drugs are unstable. In addition to this protective characteristic, hydrogel can achieve a targeted drug release because it may potentially be designed to selectively release drugs under the physiological conditions at the disease site in the body. Consequently, hydrogel has found wide application in drug delivery studies (Vashist et al., 2014).

In the other hand, hydrogel can treat water pollution as it is a massive environmental problem due to a variety of dyes used in the plastic, paper, cosmetic and textile industries are discharged in large amounts and are non-biodegradable, toxic and carcinogenic. Thus, hydrogel has been widely suggested for agricultural application during the past 40 years, in order to improve water availability for the reason that swollen hydrogel can be served as a water reservoir and will efficiently improve the plant water absorption. Nowadays, the environmental friendly hydrogel is the reason that people around the world pay increasing attention for environmental protection (Montesano et al., 2015). Similarly, according to Sahiner (2006), heavy metal ions can also be removed by hydrogel because it has hydrophilic functional groups in the hydrogel networks.

2.2   Magnetic Hydrogel

2.2.1   Properties of Magnetic Hydrogel

The magnetic hydrogel that offers additional features than hydrogel are composite materials comprised of magnetic nano- or microparticles incorporated within a polymeric matrix (Crippa et al., 2017). The magnetic hydrogel is produced as a magnetic particle which is a material composed of an inorganic magnetic component, fibers or lamellae of nanometer range embedded in an organic polymer, fill in the hydrogel. According to Souda and Sreejith (2015), the prepared magnetic hydrogel have many applications as the functional group in the hydrogel having the capacity to bind with organic and inorganic pollutants could be utilized and importantly, the combination of hydrogel network with embedded magnetic nanoparticles providing enormous surface area. Besides that, in real applications, magnetic hydrogel has a high adsorption capacity and fast separation time from a large volume of solutions besides have a better absorption capacity when compared with bare hydrogel. These can be explained by Ozay et al., (2010) as the binding affinity of metal ions on the magnetic particles is inside the hydrogel networks.

2.2.2   Application of Magnetic hydrogel

- Magnetic hydrogel as cleaning agent

As demonstrated by Ozay et al. (2010), magnetic hydrogel with an external magnetic field have low cost and rapid adsorption ability and have good potentials for the removal toxic metal ions from wastewater. The researchers have revealed that hydrogel networks with magnetic properties can effectively be utilized in the removal

of pollutants. Toxic metal ion absorbed hydrogel can be separated from the absorption media readily with a simple magnet with the magnetic responsive behavior. They observed a slight increase in the absorption capacity of the magnetic poly(2-acrylamido-2-methylpropanesulfonic acid), p(AMPS) hydrogel as metal nanoparticle that is responsible for magnetic responsiveness inside p(AMPS) hydrogel have the tendency to adsorb metal ions on their surfaces. As can be seen from Table 2.1, with the exception of Cd(II), all absorption values of magnetic hydrogel are higher than bare hydrogel.

Table 2.1: The comparison of metal ion absorption capacity of bare and magnetic p(AMPS) composite hydrogel (loading medium: 500 mL 500 mg/L) (Ozay et al., 2010).

Metal	p(AMPS) Absorption (mg Mn^+/g dry gel)	Magnetic p(AMPS) absorption (mg Mn^+/g dry gel)
Cd(II)	134.655	130.96
Co(II)	101.79	110.07
Cr(III)	66.83	76.87
Cu(II)	100.86	105.61
Fe(II)	89.64	98.28
Ni(II)	95.81	105.48
Pb(II)	120.14	126.4

Besides that, Shen et al. (1999) have proposed a fast and highly efficient method for the removal of dyes under alkaline conditions using magnetic chitosan-Fe(III) hydrogel. Adsorption could reach equilibrium faster in less

than 10 minutes in a wide range pH due to sorption of dye to chitosan-Fe(III) hydrogel. It also agreed well with Langmuir-Freundlich adsorption model with a high maximum adsorption capacity of 294.5 mg/g under pH=12. The results from the study showed that, after the desorption and regeneration, the chitosan-Fe(III) hydrogel could retain its high efficiency. The removals of a variety of anionic dyes are because the chitosan-Fe(III) hydrogel could efficiently adsorb both the acid and reactive dyes under alkaline condition. The characteristic of magnetism provides an easy and efficient way to separate the chitosan-Fe(III) hydrogel from aqueous solution.

- Magnetic Hydrogel in Biomedical Application

Magnetic hydrogel has also been produced by filling hydrogel with magnetic particles, for example, maghemite, magnetite, and cobalt-ferrite and thus make it suitable for certain biomedical applications, such as drug-delivery, enzyme immobilization or cancer therapy by the combination of controlled drug release and magnetic hyperthermia (Toth et al., 2015).

According to Crippa et al. (2017), magnetic hydrogel especially magnetic thermo-responsive hydrogel, having the ability to change phase upon magnetic stimulation, are a new class of materials that have recently attracted interest in biomedicine. It can also potentially be engineered as stimuli-responsive substrates for cell mechanobiology. Tampiere et al. (2010) had studied bone regeneration which using magnetic bio-hybrid scaffolds as magnetic hydrogel with improved physiochemical and mechanical properties. In addition, these new magnetic scaffolds are proven to provide suitable microenvironments for supporting the adhesion, growth, and proliferation of human bone marrow stem cells, based on the first results. Magnetic

guiding of cells saturated with magnetic nanoparticles inside a magnetic scaffold can effectively influence the spatial cell distribution in tissue-engineered constructions.

As for Ting et al. (2009), they fabricated magnetic hydrogel by chemically cross-linking of gelatin hydrogel and Fe_3O_4 nanoparticles, a responsive composite that can be applied as a drug delivery system by magnetic fields (MF). One possible application of magnetically and thermally responsive smart nanomaterials which pertain to remotely controlled drug delivery is illustrated in Figure 2.2.
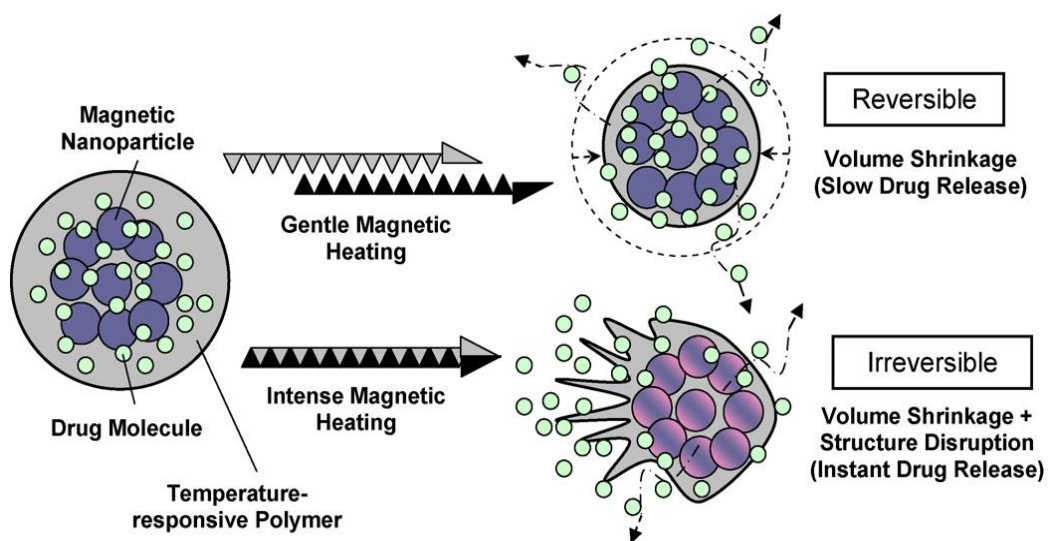
Figure 2.2: Two drug release mechanisms under magnetic heating. Gentle magnetic heating causes temperature-responsive polymer to shrink, squeezing drug out from the nanoparticle. Intense magnetic heating additionally ruptures the nanoparticle, triggering a burst-like drug release (Ting et al., 2009)

The hard magnetic material of choice is the iron oxide in this study, which is relatively safe for biomedical applications and can be readily synthesized in a form of small particles to be embedded into the soft material which is hydrogel. Moreover, by using a high-frequency field, remote magnetic heating of iron oxide becomes possible

thereby converting a magnetic stimulus to a thermal stimulus. Applications of magnetically and thermally responsive nanocolloids in medicine and biotechnology such as drug delivery and enzyme immobilization or separation.

Similarly, observation via magnetometry shows that the absence of hysteresis loops and coercivity which suggests that magnetic hydrogel is useful for remote-controlled drug release, as demonstrated by the magnetic-field-induced release of curcumin.

2.2.3   Technology To Synthesis Magnetic Hydrogel

- Free Radical Cross Linking Polymerization

This technology is studied by Souda and Sreejith (2015) where the hydrogel is typically prepared by the free radical crosslinking polymerization mechanism. The thermally dissociating initiator, heated to about 60°C decomposes and produces sulfate radicals to initiate the copolymerization reaction. In the presence of a crosslinker, these free radicals then start to copolymerize the monomers acrylic acid (AA), maleic acid (MA) and 2-Acrylamido-2-methyl-1-propanesulphonic acid (AMPS). All these monomers can also produce free radicals and start to a chain reaction due to double bonds. The fraction of crosslinker present in the reaction mixture controlled the degree of cross-linking. The electrostatic forces created in the hydrogel are responsible for the stability of hydrogel loaded with iron ions in comparison to hydrogel. The hydrogel loaded with iron ions were treated with sodium hydroxide then the magnetic nanoparticles formed are stabilized inside the hydrogel networks. The free space within the hydrogel networks was found to decrease during

the particles formation and thus the swelling behavior of magnetic hydrogel was noted to be low as compared to that of the pure hydrogel. The magnetic hydrogel that has the Fe_3O_4 particles randomly aggregated structure throughout the gel.
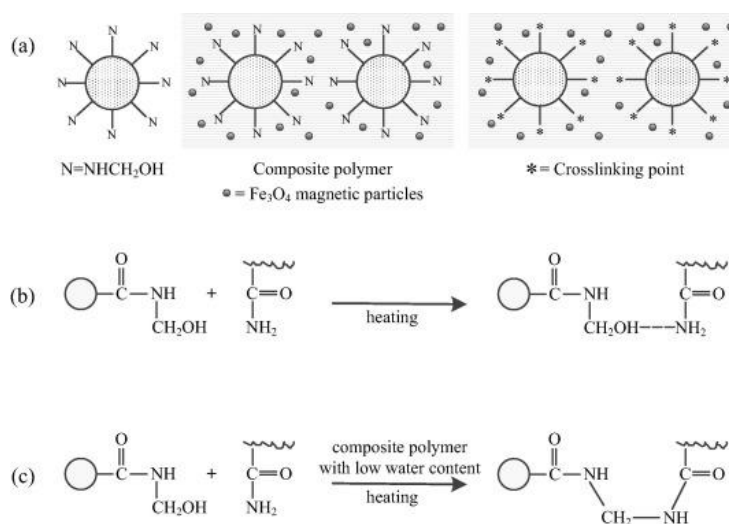

Figure 2.3: Schematic of the formation of magnetic hydrogel and polymer crosslinked; (a) Synthesis of magnetic hydrogel, (b) Formation of hydrogen bond and (c) Formation of covalent bond (Zhao et al., 2015)

A study done by Zhao et al. (2015), magnetic hydrogel is synthesis by free radical cross-linking polymerization. The magnetic hydrogel (MH) was prepared by three continuous processes named preparation of reactive microgels that contain hydroxymethyl, preparation of composite polymer microgels and preparation of magnetic hydrogel (Figure 2.3(a)). Microgel hydroxymethyl has high activity and easily reacts with acylamino. Figure 2.3(b) showed the formation of hydrogen bond while the formation of covalent bond was shown in Figure 2.3(c). Potential crosslinking agent, reactive microgels with hydroxymethyl, which were uniformly dispersed in aqueous solution of Acrylamide (AM) and 2-acrylamide-dimethyl propyl sulfonic acid (AMPS). Then, composite polymer microgels were obtained by free radical polymerization. Generally, the polymerization temperature was controlled

lower than 60°C where reactive microgels and Fe_3O_4 magnetic particle did not participate in the reaction. Finally, hydroxymethyl of reactive microgels reacted with active groups by heating as shown in Figure 2.3(b) and (c). Then the magnetic hydrogel was got.

- Co-precipitation

Studies by Shen et al. (1999) shows that aqueous magnetic fluids were synthesized by a sequential process involving the chemical co-precipitation of Fe(II) and Fe(III) salts with ammonium hydroxide (NH_4OH) then followed by resuspension of the ultrafine particles in water using fatty acids. This procedure will produce Fe_3O_4 nanoparticles that are stabilized against agglomeration by bilayers of n-alkanoic acids with 9 to 13 carbons encapsulating the metal particles. The magnetic properties and particle size and size distributions of these magnetic fluids indicate the formation of single-domain nanoparticles of mean diameter ~9.3 and ~7.5 nm, respectively. Thermogravimetric analysis measurements showed the existence of two distinct populations of surfactants on the particle surface, which was consistent with highly organized surfactant bilayer structures. Differential scanning calorimetry indicated the presence of a phase transition for the bilayer-coated particles that suggests partial interpenetration of the hydrocarbon tails of the primary and secondary surfactants.

2.3 Cellulose Waste

2.3.1 Composition of Cellulose Waste

Cellulose wastes which are residues from agricultural activities and industrial food processing are produced worldwide in great amounts, which could be measured in many billions of tons (Petre et al., 1999). In 2014, the total waste generated by the Europian Union by all economic activities and households amounted to 2598 million tonnes. As shown in Figure 2.4 is the classification of waste generated in 2014. Cellulose waste is classified is forestry wastes which bring to 1.4% of waste generated which amounts to 36372000 tonnes (Eurostat, 2016).
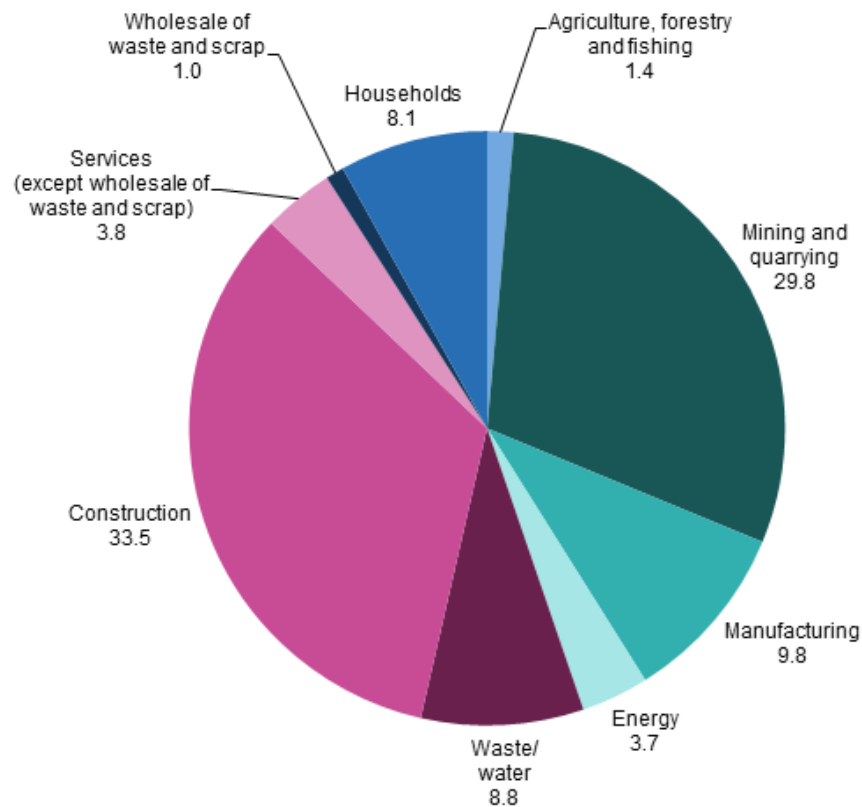

Figure 2.4: Waste generation by economic activities and households (Eurostat, 2016)

Basically, according to Petre et al. (1999), the cellulose is the most widely distributed skeletal polysaccharide and represents about 50% of the cell wall material

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of plants. The cellulose and hemicellulose comprise the major part of all green plants. Terms such as 'cellulosic wastes' or simply 'cellulosics' for those materials which are produced especially as agricultural crop residues, fruit and vegetable wastes from industrial processing, and other solid wastes from canned food and drinks industries. 'elementary fibrils' are the cellulose molecules that is composed of longer slender bundles of long chains of β-d-glucopyranose residues linked by 1-4 glucosidic bonds. Within each elementary fibrils, the cellulose molecules are laterally bound and the adjacent molecules run with various degrees of orientation, in parallel opposite direction. Besides cellulose, the cellulosic waste materials also contain hemicellulose, lignin, extractives, and inorganic compounds. The component of cellulosic waste from crop residues and other agricultural wastes are 31–60% cellulose, 11–38% pentosans, and 12–28% lignin.

Cellulose is defined as a linear polymer of anhydroglucose units linked at C1 and C4 atoms by a β -glucoside bond. The degree of polymerisation in cellulose molecule is found to be a considerably varying one. Various models of cellulose structure have been proposed by Chang (1971).
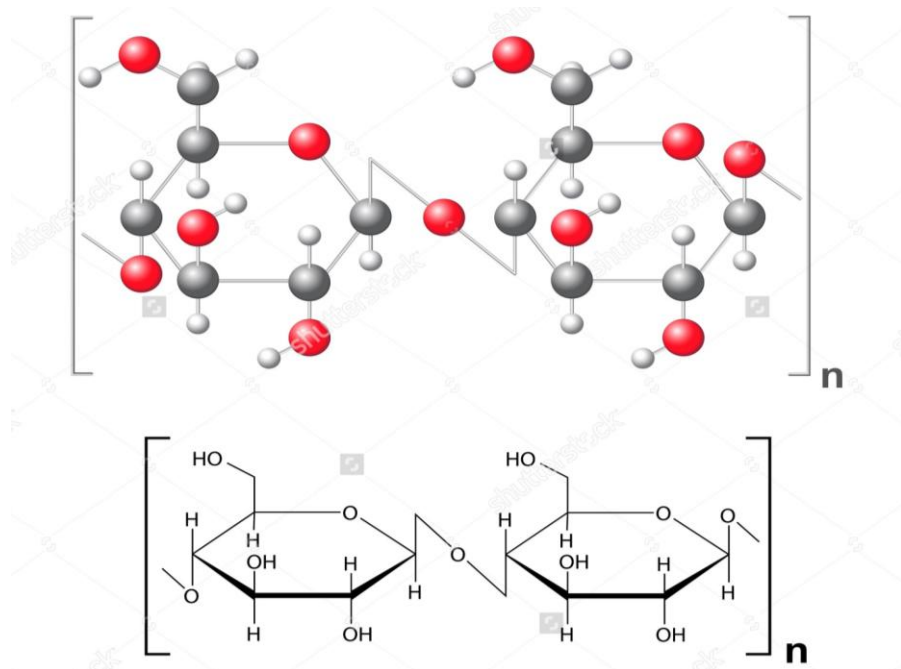
Figure 2.5: Models of cellulose structure

Cellulose is soluble in a number of solvents, including concentrated acids and inorganic solvent solutions but insoluble in water. Cellulose itself have high molecular weight, a high degree of structural order, insolubility, and low surface area make it the least degradable natural polymers. The plant materials more stable to chemicals and enzymes due to its association with lignin and hemicelluloses. Four types of degradation have been characterized, namely hydrolytic, oxidative, microbial, and mechanical degradation.

2.3.2 Utilization of Cellulose Waste

Cellulose is the world's most abundant renewable resource polymer. Cellulosic wastes are now recognized as an underutilized renewable resource for both materials and energy recovery rather than a solid waste disposal problem. Its main uses are in the form of wood for construction, furniture, papers, boards, clothes, foods, and feeds (Brenner et al., 1979).

Brenner et al. (1979) from his paper had mentioned that from the agricultural farms, plantations, and orchards, the cellulosic residues generated in the form of stalks, straws, stems, leaves, cobs, chaffs, bunches, stumps, and stubbles, damaged grains, fruits, vegetables, etc. The major cellulosic wastes from food industries include damaged fruits, vegetables and grains, and post-processing residues, like skins, peels, seeds, leaves, bunches, husks, bagasse, vinasse, pomace, etc. These cellulose wastes have an immense potential to be utilized for the production and recovery of several products and ingredients in food application.

Similarly, cellulose waste plays an important function in petrochemical industries. The inexpensive and renewable cellulosic wastes which have a wide availability of very large amounts of has revived consideration of their possible use as a feedstock to replace at least partially petroleum crudes for the production of fuels, petrochemicals and even synthetic proteins (Brenner et al., 1979).

2.4   Sawdust

2.4.1   Properties of Sawdust

Wood is the basic material for furniture, interior decorating, and construction industries. Waste wood, waste paper, and waste plastics are major components of municipal solid waste (MSW), that offers great opportunities for making recycled ingredients into wood fiber and plastic composites. Wood fibers can be recycled by using sawdust where it provides an additional use and thus further reduces waste in landfills. (Brostow et al., 2016)

Sawdust, mostly known as a by-product of the furniture industry and produced as a papermaking industrial waste without commercial value in very large amount every year, is rich in lignin and cellulose. Sawdust as biologic materials, together with rice husk and wheat drugs contains a high calorific value, the use of which as the conditioner can greatly improve the heat value of sludge cake. This is because, according to Liu et al. (2017), results from the study shows that the sawdust conditioning superiorities in sludge cake air drying and calorific value increase. In addition, the moisture content of sludge cake can be greatly reduced by sawdust conditioning, which could also decrease sludge compressibility, reduce bound water content, improve the porosity of sludge cake, but scarcely influence sludge particle size. Moreover, during natural air drying, sawdust conditioning presented high efficiency in further dewatering of sludge cake.

As shown in Figure 2.6, sludge dewatering rate could be enhanced to some extent by the addition of sawdust and quickened with the increase of its dosage. Therefore, results indicate sludge conditioning with sawdust can efficiently decrease the moisture content of sludge cake, but only finitely accelerate dewatering rate.
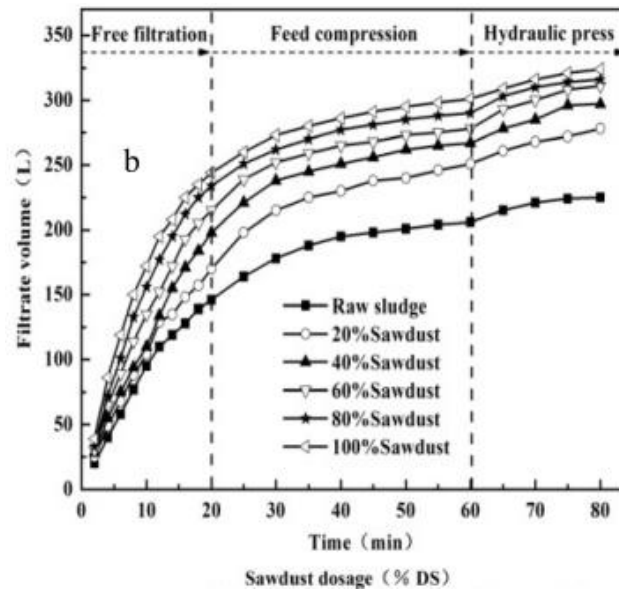

Figure 2.6: Dewatering rates and moisture content of the sludge cake conditioned by amount of sawdust used (Liu et al., 2017)

2.4.2   Uses of Sawdust in Industry

Sawdust as the by-products and wastes of agricultural and wood industries are a major source of the biomass used in the production of biofuels and biomaterials. The majority of pellets on the world market are produced from sawdust. To obtain and improve the properties and quality of pellets, biomass materials are frequently mixed. Many types of research had been done to produce pellet from a combination of sawdust. Lee et al. (2013) had examined the influence of species, wood particle size, moisture content, pelletizing temperature and time on the durability of larch and