TREATMENT OF POME VIA CHITOSAN BASED FLOCCULATION: A STUDY ON VARIABLE pH AND TEMPERATURE

NORIEDAH BT SOFIAN

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Faculty of Chemical & Natural Resources Engineering
Universiti Malaysia Pahang

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ABSTRACT

Palm oil mill effluent (POME) is one of the major problematic oily wastewaters in Malaysia. POME contains 4,000 mg/L of oil and grease, which is relatively high compared to the limit of only 50 mg/L set by the Malaysian Department of Environment. In this study, chitosan, poly-b-(1,4)-2-acetamido-2-deoxy-D-glucose (N-deacetylated) was used as an adsorbent to adsorb the excess oil from oily wastewater. Besides, chitosan is a biodegradable cationic biopolymer achieved by the extensive deacetylation of chitin obtained from prawn shell waste. The study was conducted by using jar-test apparatus to evaluate the oil removal performance via chitosan. The parameters studied were the effect of variation of pH and temperatures; as well as monitoring of settling rate. From the results, it showed that at pH 5 and optimum temperature of 60 ^{o}C, provided the most suitable conditions for the residue oil removal with employing the settling rate for 120 minutes. In conclusion, chitosan has a potential in removing oil from oily wastewater.

ABSTRAK

Efluen industri minyak sawit (EIMS) merupakan satu masalah air buangan yang berminyak di dalam Malaysia. Efluen industri minyak sawit mengandungi 4000 mg/L akan minyak dan gris, yang mana secara relatifnya tinggi berbanding dengan had 50 mg/L yang ditetapkan oleh Kementerian Alam Sekitar, Malaysia. Di dalam penyelidikan ini, kitosan, poli-b-(1,4)-2-amino-2-deoksi-D-glukan (N-deasitilated) telah digunakan sebagai salah satu alat penyerap bagi menyerap lebihan minyak daripada minyak air buangan. Selain itu juga, kitosan ialah satu kationik biodegradsi biopolimer tercapai dengan deasilitasi akan kitin yang diperolehi daripada buangan kulit udang. Penyelidikan telah dijalankan dengan menggunakan alatan ujian balang bagi menilai perlaksanaan lebihan minyak dengan menggunakan kitosan. Parameter yang telah diselidiki ialah akibat variasi pH dan suhu; dan memantau kadar pemendapan. Hasil yang telah didapati menunjukkan bahawa pH 5 dan suhu optimum 60 ^{o}C, menunjukkan keadaan yang sangat sesuai bagi penyingkiran sisa minyak dengan memanfaatkan kadar pemendapan selama 120 minit. Kesimpulannya, kitosan mempunyai potensi dalam penyingkiran minyak daripada air buangan yang berminyak.

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LIST OF SYMBOLS

POME	Palm Oil Mill Effluent
BOD	Biochemical Oxygen Demand
CPO	Crude Palm Oil
COD	Chemical Oxygen Demand
EFB	Empty Fruity Bunches
MPOB	Malaysia Palm Oil Board
TS	Total Solids
SS	Suspended Solids
TN	Total Nitrogen
WSP	Waste Stabilization Ponds
DOE	Department of Environment
%DA	Degree of Deacetylation
^{o}C	Degree Celsius
mL	Milliliter
g	Gram
min	Minute
nm	Nanometer
mPa·S	mili pascal-second
w/w.	(an abbreviation for "by weight”) the concentration of a substance in a mixture or solution
L	Litres
rpm	Revolutions per minutes
mg/L	Concentration

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Oil palm (Elaeis guineensis Jacq.) was first reported by the Portuguese sailor Eannes in 1434. The oil palm is native to West and Central Africa where its food use dates back to over 5000 years. Its botanical classification is derived from the Greek elaion (oil) and the specific name of guineensis is indicative of its origin from the equatorial Guinea coast. In 1763, Nicholaas Jacquin produced one of the earliest illustrations of the oil palm tree and he is remembered in its scientific name (Hartley, C.W.S. The Oil Palm 1988 3rd edn).

Figure 1.1 Palm Oil Tree and Fresh Fruit Bunch (FFB)

This tree (Figure 1.1) produces one of the most popular edible oils in the world – a versatile oil of superb nutritional value. It is the most prolific of all oil plants and in commercial terms the one which offers major prospects of development. Palm oil is commercially used in soap, ointments, cosmetics, detergents, and machinery lubricants. It is also used worldwide as cooking oil, shortening, and margarine.

To date, Malaysia is the largest producer and exporter of palm oil products in the world. In 2003, Malaysia contributed to 13.4 million tons or 49% of world production and 12.2 million tons or 58% of total world exports. However, this important economic activity generates an enormous amount of effluent which could pollute the environment if not properly treated. It is estimated that for every ton of crude oil is produced, about 2.5 – 3.5 ton of palm oil mill effluent (POME) is generated (Ahmad *et al.,* 2005). In palm oil mills, liquid effluent is mainly generated from sterilization and clarification processes in which large amounts of stream and/or hot water are used. The mixed effluent is commonly known as POME.

These wastes contain very high volumes of oil-in-water emulsions as their basic contaminant. This emulsified oil droplets are sheltered from spontaneous coalescence into larger flocs, thus making oil separation by simple gravity a difficult and time consuming process (Zouboulis and Avranas, 2000). Reducing the environmental loading from oily wastes, decreasing processing costs and other products which utilize residue are strong drives for oily waste treatments.

Realizing the escalating situation, measures to counter pollution from POME have been deployed. Thus, numerous methods have been used to remove residue from wastewaters such as adsorption, coagulation, flocculation, electro-coagulation and flotation (Andrew *et.al.*, 2000).

Flocculation is the transport steps that bring the collisions between destabilized colloid particles need to form the larger particles than those obtained by coagulation and can be removed readily by settling and then filtration. Flocculants, or flocculating agents, are chemicals that are used to promote flocculation by causing colloids and other suspended particles in liquids to aggregate, forming a floc. Flocculants are used in water treatment processes to improve the sedimentation or filterability of small particles.

Chitosan is one of the natural products that are used as flocculants. Chitosan, poly (D-glucosamine) a natural deacetylated marine polymer has been used in a variety of practical fields including wastewater management, pharmacology, biochemistry, and biomedical (Majeti, 2000; Feng *et al*., 2000). Chitosan has excellent properties such as biodegradability, hydrophilicity, biocompability, adsorption property, flocculating ability, polyelectrolisity, antibacterial property and its capacity of regeneration in a number of applications (Majeti, 2000; Feng *et al*., 2000). Its largest use is as a non-toxic flocculent in the treatment of organic polluted wastewaters and as a chelating agent for toxic (heavy and reactive) metals (An *et al*., 2001). Chitosan is believed to be the best natural adsorbent to remove oil from wastewater.

1.2 Problem Statement

Palm oil industries are facing tremendous challenges to meet the stringent environmental regulations. Besides earning a remarkable profit from the palm oil production, palm oil processing mills discharge vast amount of effluent (Ahmad A.L *et al.,* 2005) which known as palm oil mill effluent (POME). Hassan *et al.* (2004) reported that for every tonne of oil palm fresh fruit bunch, it is estimated that 0.5 to 0.75 tonnes of POME will be discharged from the mill. In the year 2004 alone, more than million tonnes of POME was generated from 372 mills in Malaysia.

One of the main ingredients in palm oil mill effluent (POME) that causes severe problems is its residue oil. POME is a colloidal suspension containing 95–96% water, 0.6–0.7% oil and grease and 4–5% total solids. It is a thick, brown liquid with a discharge temperature of between 80°C and 90°C, being fairly acidic with a pH value in the range 4.0–5.0.

Residue oil is a major problem in oily wastewaters especially in vegetable oil mill effluents and has to be removed in order to prevent interfaces being generated in water-treatment units, to avoid problems in the biological treatment stages and to comply with water-discharge requirements. Thani *et al*. (1999) reported that palm oil mill is typically generate a large quantity of oily effluent with extremely high organic content classified it as an environmental issue.

Normally, emulsified oil droplets do not undergo spontaneous coalescence into larger flocs, making oil separation by simple gravity methods a difficult and time-consuming process). Hence, in this study, a natural polyelectrolyte, i.e. chitosan will be used to floc the residue oil in POME. Although many studies on adsorption using chitosan were done, the roles of chitosan in adsorbing residue oil were rare.

Numerous methods such as adsorption, flocculation, electrocoagulation and flotation (Andrew *et al*., 2000) have been used to remove residue oil from wastewaters. Previous design of the POME treatment is much concerned on reducing the organic removal (BOD) in order to comply with discharge limit standard. Therefore, this study will investigated the used of flocculation for POME treatment.

1.3 Objective of the Study

The main objective of this study is:

1. To study the treatment of Palm Oil Mill Effluent (POME) via chitosan based flocculation.

Scope of the Study

There are three scopes of study that identified to achieve the objective mentioned above and are listed as below:

1. To study the effect of pH and temperature in treating oily wastewater from POME.
2. To study the settling rate of the purpose treatment.
3. To evaluate the improvement of water quality before and after treatment.

CHAPTER 2

LITERATURE REVIEW

2.1 Palm Oil Mill Effluent (POME)

2.1.1 Introduction

Palm oil is an important crop in Malaysia and the industry is one of the largest agro-based industries in Malaysia (Wong *et al*., 2002). The process to extract the oil requires significantly large quantities of water to steam sterilize the palm fruit bunches and clarify the extracted oil. It is estimated that for 1 tonne of crude palm oil (CPO) produced, 5-7.5 tonnes of water are required, and more than 50% of the water will end up as palm oil mill effluent (POME) (Abdul Latif *et al*., 2003). Therefore, it is very crucial to give special attention to the adverse environmental impact from the palm oil industry.

POME is brown slurry composed of 4-5% solids, mainly organic, 0.5-1% residual oil, and about 95% water (Onyia *et al*., 2001). The raw or partially treated POME has an extremely high content of degradable organic matter, which is due in part to the presence of unrecovered palm oil. This highly polluting wastewater can therefore cause severe pollution of waterways due to oxygen depletion and other related effects.

It is an important source of inland water pollution when released into local rivers or lakes without treatment. POME contains high lignocellulolic wastes with a mixture of carbohydrates and oil. Chemical oxygen demand (COD) and biochemical oxygen demand (BOD) of POME are very high and COD values greater than 80,000mgl^{-1} are frequently reported. Incomplete extraction of palm oil from the palm nut can increase COD values substantially (Oswal *et al*., 2002). Table 2.1 shows the refined characteristics of raw POME (Ma, 1999, 2000).

Thus, the challenge of balancing the POME into a more environmental friendly waste requires a sound and efficient treatment and disposal approach.

Table 2.1: Characteristics of POME (Ma, 2000)

Parameter	**Concentration (mg/L)**	**Element**	**Concentration (mg/L)**
Oil and grease	4000-6000	Phosphorus	180
Biochemical oxygen demand	25 000	Potassium	2270
Chemical oxygen demand	50 000	Calcium	439
Total solid	40 500	Boron	7.6
Suspended solids	18 000	Iron	46.5
Total volatile solids	34 000	Manganese	2
Ammonicals nitrogen	35	Copper	0.89
Total nitrogen	750	Magnesium	615
		Zinc	2.3

2.2 Definition of POME

A typical palm oil mill releases liquid effluent, known as palm oil mill effluent (POME), gaseous emissions from boilers and incinerators, solid waste materials and by-products that include empty fruity bunches (EFB), potash ash, palm kernel, fiber and shells (Wong *et al*., 2002). POME is complex in nature and content highly organic matter. At any conventional palm oil mill processes, it has been estimated each tonnes of crude palm oil produced, approximate 2.5 to 3.5 m3 of POME are generated (Ahmad *et al*., 2003). These wastes, if not disposed properly, will cause negative and deleterious effect to the environment as well as human beings.

POME is a colloidal suspension that contains 95–96% of water, 0.6–0.7% of oil and grease and 4–5% of total solids including 2–4% suspended solids originated from the mixture of sterilized condensate, separator sludge and hydrocyclone wastewater (Ma, 2000). In most mills, these three wastewater streams are combined together resulting in viscous brown liquid containing fine suspended solids.

POME possesses a few characteristics as which have been stated by the Malaysian Department of the Environment. Characteristics of POME and its respective standard discharge limit by the Malaysian Department of the Environment are shown in Table 2.2 below.

Table 2.2: Characteristics of POME and its respective DoE standard discharge limit (Abdul Latif *et al*., 2003)

Parameter	**Concentration, mg/L**	**DoE Standard limit, mg/L**
pH	4.7	5-9
Oil & Grease	4,000	50
Biochemical oxygen demand (BOD)	25,000	100
Chemical oxygen demand (COD)	50,000	50
Total solid (TS)	40,500	-
Suspended solids (SS)	18,000	400
Total nitrogen (TN)	750	150

2.3 Palm Oil Mill Effluent Technology Treatment

POME in general is a combination of wastewaters that are generated and discharged from three main sources, i.e. sludge clarification, sterilizer condensate and hydrocyclone which contribute about 60%, 36% and 4% of total POME, respectively (MPOB, 2003). There are other minor sources of relatively clean wastewater that might be included in the combined POME, which is piped to the wastewater treatment plant. These include turbine, cooling tower and stream condensates, boiler blowdown, overflows form vacuum dryers and some floor washings. The volume of combined POME discharge depends to a large extent on the milling operations.

POME consists of essentially organics and biodegradable compounds. The biodegradability is influenced by the extent of cellulosic materials present such as the palm fibre residues as the residual oil content. The effluent treatment technologies for POME are, there, invariably biological process.

The organic content of POME is generally biodegradable and treatment required could be based on anaerobic and facultative processes. The processes are essentially biochemical and rely on the enhanced growth and metabolic activities of suitable microorganisms to transform the organic matter into simple end product such as methane, carbon dioxide and hydrogen sulphide, and water. Microorganisms involved are primarily bacteria and algae which result in the production of excess biomass (microbial cells) that needs to be disposed off in the form of sludge. This sludge can be appropriately land applied in the oil palm plantation as soil conditioner (MPOB, 2003).

The waste stabilization ponds (WSP) system, which essentially consists of anaerobic, aerobic and/or facultative ponds or lagoons, is the most commonly used (more than 85%) by Malaysian palm oil mills (DOE, 1999). In this system, the anaerobic treatment process takes place in anaerobic ponds or lagoons. Due to slow flow for WSP and excessive concentration of nutrients in POME, algal growth is inevitable. In addition, odour formation would occur especially in anaerobic ponds.

2.4 Flocculation

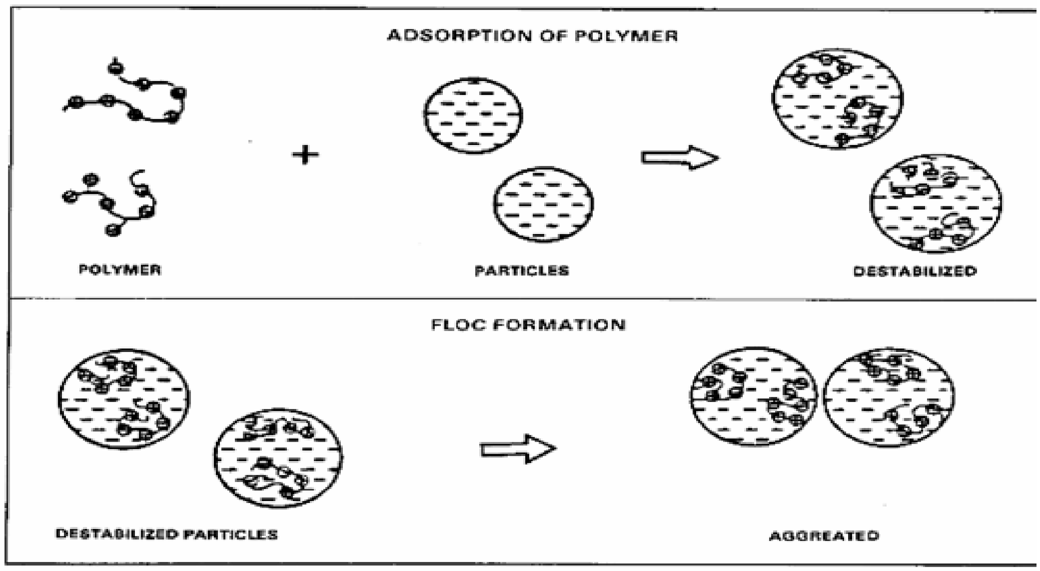

Figure 2.1 Floc formation process (globalsecurity.nd)

Flocculation is the action of bridging between the flocs, and binding the particles into large agglomerates. Bridging occurs when segments of the polymer chain adsorb on different particles and help particles aggregate (Figure 2.1). The majority of particles that are suspended in water (called colloids) carry a negative charge, which causes them to repel each other. This repulsion allows the particles to retain their light weight, making it hard form hem to settle out of the water. The particles are force down to the bottom of the water by increase their mass.

A cationic flocculants will react against a negatively charged suspension, adsorbing on the particles, causing destabilization either by bridging or charge neutralization, thereby reducing the repulsion, and allowing for the conglomeration of colloidal particles into a floc that is heavy enough to be pushed to the bottom of the water by gravity.

In this process it is essential that the flocculants to be added by slow and gentle mixing to allow for contact between the small flocs and to agglomerate them into larger particles. The newly formed agglomerated particles are quite fragile and can be broken apart by shear forces during mixing. Flocculation is conducted under conditions of lower mixing intensity to prevent shear and degradation of the growing floc particles.

Flocculation also refers to a process where a solute comes out of solution in the form of floc or "flakes". The term is also used to refer to the process by which fine particulates are caused to clump together into floc. The floc may then float to the top of the liquid, settle to the bottom of the liquid, or can be readily filtered from the liquid. In flocculation, the dosage of flocculants is also important to avoid problems in settling and clarification. Cationic polymers themselves are lighter than water. As a result, increasing the dosage will increase the tendency of the floc to float and not settle.

Once suspended particles are flocculated into larger particles, they can usually be removed from the liquid by sedimentation, provided that a sufficient density difference exists between the suspended matter and the liquid. Such particles can also be removed or separated by media filtration, straining or floatation. When a filtering process is used, the addition of a flocculant may not be required since the particles formed by the coagulation reaction may be of sufficient size to allow removal. The flocculation reaction not only increases the size of the floc particles to settle them faster, but also affects the physical nature of the floc, making these particles less gelatinous and thereby easier to dewater.

2.4.1 Flocculation Principles

In flocculation relatively long chain, synthetic polymers (polyelectrolytes) (Figure 2.2) are used to overcome the potential energy barrier preventing the spontaneous aggregation of particles. Whilst the presence of the correct dosage and type of polymer is important, the degree of flocculation is also dependent on a number of others factors including the amount of energy input during agitation.

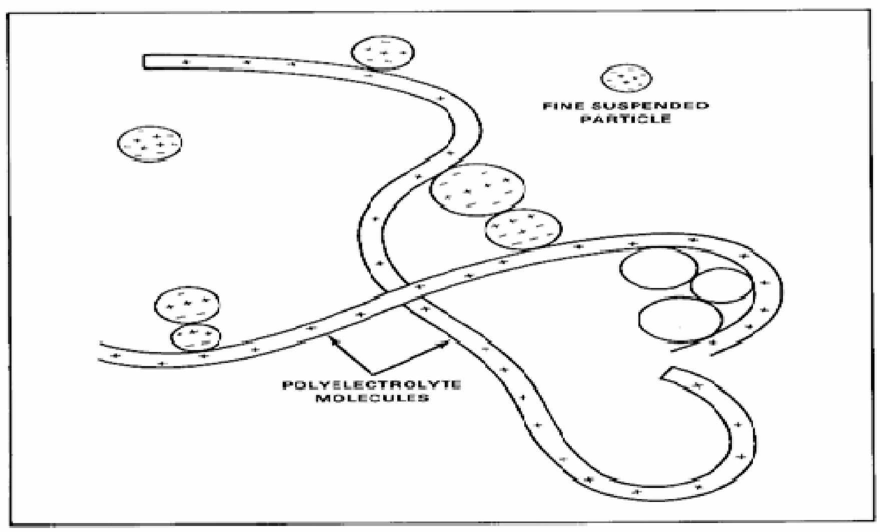

Figure 2.2 Forming a floc particle (globalsecurity.nd)

The polyelectrolytes used to promote flocculation contain functional groups along their 'backbone' which may or may not carry a charge. If the groups are charged they can give the chain an anionic (-ve charge) character, a cationic (+ve charge) character, or in some instances an amphoteric character exhibiting both anionic and cationic charges. The intensity of the charges is dependent on the degree of ionization of the functional group, the degree of co-polymerization and/or the amount of substituted groups in the polymer structure. The extent of polymerization of the polyelectrolyte is characterized by the molecular weight and high molecular weights are usually synonymous with long chains. Functional groups in the structure also constitute sites at which the polymer may adsorb onto a particle surface.

2.5 Flocculants

Flocculants, or flocculating agents, are chemicals that are used to promote flocculation by causing colloids and other suspended particles in liquids to aggregate, forming a floc. Flocculants are used in water treatment processes to improve the sedimentation or filterability of small particles. For example, a flocculant may be used in swimming pool or drinking water filtration to aid removal of microscopic particles which would otherwise cause the water to be cloudy and which would be difficult or impossible to remove by filtration alone.

Many flocculants are multivalent cations such as aluminium, iron, calcium or magnesium. These positively charged molecules interact with negatively charged particles and molecules to reduce the barriers to aggregation. In addition, many of these chemicals, under appropriate pH and other conditions, react with water to form insoluble hydroxides which, upon precipitating, link together to form long chains or meshes, physically trapping small particles into the larger floc.

Flocculant is used for separating treated water and suspended solids in the wastewater treatment plant. By adding this chemical, suspended solids are sedimented with flocculants and get the clearized water. The flocculants are classified to into three kinds:

1. Inorganic flocculants; aluminum sulfate and polyalminum chlorides.
2. Organic synthesis high polymers; polyacrylic acid, polyacrylamide derivatives.
3. Naturally occurring flocculants; chitosan, sodium arginate and Moringa oleifera seeds.

Long-chain polymer flocculants, such as modified polyacrylamides, are manufactured and sold by the flocculant producing business. Modified Polyacrylamides can be supplied in dry or liquid form for use in the flocculation process. The most common liquid polyacrylamide is supplied as an emulsion with 10-40% actives and the rest is a carrier fluid, surfactants and latex. Emulsion polymers require activation to invert the emulsion and allow the electrolyte groups to be exposed. Other factors such as pH, temperature, and salinity can induce flocculation or influence flocculation rates.

2.6 Chitosan as Flocculant

2.6.1 Introduction

Chitosans are polysaccharides that result after the N-deacetylation of chitin (Figure 2.3), (Hirano, 2000; Hudson and Smith, 1998). Chemically they are derivatives of cellulose with 2-acetamido-groups instead of 2-hydroxy groups. They consist of β-(1-4)-D-glucosamine. The process of N-deacetylation of chitin can be controlled in its conditions, and according to the conditions different deacetylated chitosans result (40%-98%) (Pavlath *et al*., 1996). Furthermore, the products vary in their degree of polymerization. Chitosan powders have been determined to be crystalline up to 71% deacetylation, further deacetylation leads to a strong decrease in crystallinity and starting from 89% deacetylation crystallinity increases (Luyen and Huong, 1996).

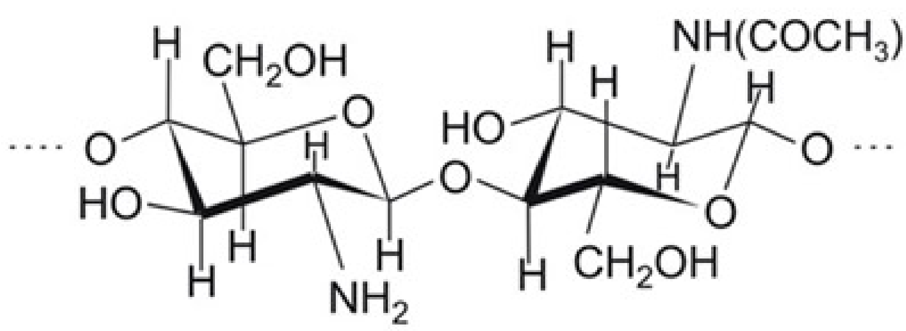

Figure 2.3 Chemical structure of chitosan

Chitin is the second most common polymer and is naturally present in crustacean shells and fungi. The shells of crab, shrimps, and lobster are waste products of the food industry and can be used to produce chitosans (Hudson and Smith, 1998).

Chitosans are nontoxic, biocompatible, and biodegradable and have been widely used for pharmaceutical purposes, and for other purposes such as clarification of waste water, in food products, in feed ingredients, and as a wet strength additive in the paper industry (Hudson and Smith, 1998; Paul and Sharma, 2000).

Chitosan is a white amorphous solid which is insoluble in water but soluble in very dilute acids such as acetic, formic, etc. However, its solutions undergo slow biodegradation (Chihpin *et al*., 2000). It is second only to cellulose in abundance. Moreover, chitosan is a fiber-like substance derived from chitin, a polysaccharide found in the exoskeletons of crabs, shrimp and other shellfish. It possesses a positive ionic charge, which gives it the ability to chemically bond with negatively charged fats, lipids and bile.

2.6.2 Manufacture and Properties

Chitosan has the highest sorption capacity for several metal ions (Deshpande, 1986) among the many other low cost absorbents identified (Olin et al. 1996; Bailey *et al.,* 1997, Bailey *et al.,* 1999). Chitin (2-acetamido-2-deoxy-β-Dglucose-(N-acetylglucan) is the main structural component of molluscs, insects, crustaceans, fungi, algae and marine invertebrates like crabs and shrimps (Deshpande, 1986; Chen and Chang, 1994; Ilyina *et al.,* 1995).

Worldwide, the solid waste from processing of shellfish, crabs, shrimps and krill constitutes large amount of chitinaceous waste. Chitosan (2-acetamido-2-deoxy-β-D-glucose-(Nacetylglucosamine) is a partially deacetylated polymer of chitin and is usually prepared from chitin by deacetylation with a strong alkaline solution as shown in Figure 2.4. The degree of deacetylation (%DA) can be determined by NMR spectroscopy, and the %DA in commercial chitosans is in the range 60-100 %.

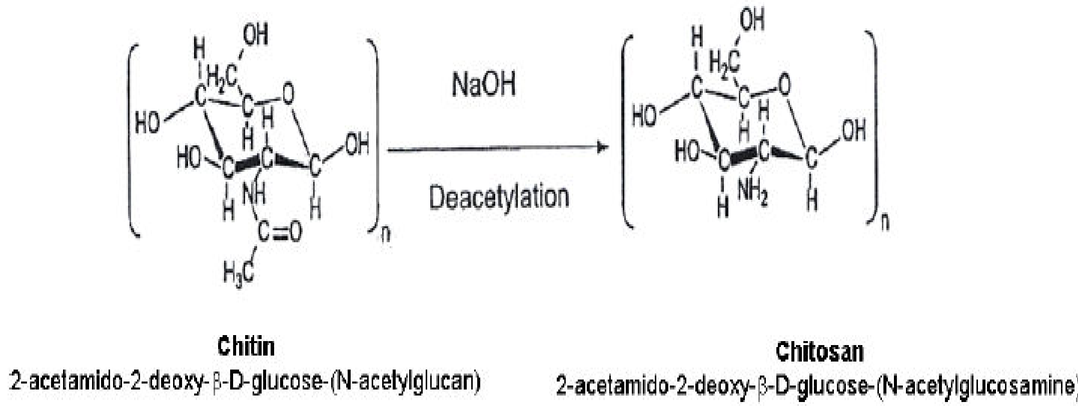

Figure 2.4 Conversion of chitin to chitosan by deacetylation

Chitosan chelates five to six times greater amounts of metals than chitin. This is attributed to the free amino groups exposed in chitosan because of deacetylation of chitin (Yang and Zall, 1984). The amino group in chitosan has a pKa value of ~6.5, thus, chitosan is positively charged and soluble in acidic to neutral solution with a charge density dependent on pH and the %DA-value. In other words, chitosan is bioadhesive and readily binds to negatively charged surfaces such as mucosal membranes. Chitosan enhances the transport of polar drugs across epithelial surfaces, and is biocompatible and biodegradable. Purified qualities of chitosans are available for biomedical applications.

Besides, the biosorbent material, chitosan, is slightly soluble at low pH and poses problems for developing commercial applications. It is also soft and has a tendency to agglomerate or form a gel in aqueous solutions. In addition, the active binding sites of chitosan are not readily available for sorption. Transport of the metal contaminants to the binding sites plays a very important role in process design. Therefore, it is necessary