TREATMENT OF POME VIA CHITOSAN BASED FLOCCULATION: A STUDY ON THE DEGREE OF DEACETYLATION OF CHITOSAN

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A dissertation submitted in fulfillment of the
requirements for the award of Bachelor's Degree

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MAY 2008

"I hereby declare that I have read this dissertation and in my opinion this dissertation is sufficient in terms of scope and quality for the award of the Bachelor's Degree in Chemical Engineering"

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I declare that this thesis entitled "Treatment of POME via Chitosan Based Flocculation: A study on the degree of deacetylation of chitosan" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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To my beloved mother, late father and those who know me. Love you all.

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ABSTRACT

This dissertation is about treatment of palm oil mill effluent (POME) wastewater via chitosan based flocculation and the degree of deacetylation will be studied. Chitosan is so-called deacetylated chitin and is well-known as one of the ingredient used in slimming product because of its ability to absorp oil and because of that it is suitable to use in treatment of POME wastewater. One of the methods used to treat POME wastewater is using membrane technology. This method even though with high separation capability, requires a lot of process and expensive. It is thus justifiable that this study is conducted to study the effect of varying the degree of deacetylation (DDA) of chitosan in treatment of POME wastewater. The molar percentage, time and temperature of the treatment were varied within the range of 30 to 70% NaOH concentration, 40 to 90^{o}C and 5hr to 3 days respectively. The method used to treat the chitin is one step deacetylation process by soaking the chitin in different treatment conditions. The DDA was later determined by using the absorbance value from testing the chitosan with Fourier Transform Infrared Spectroscopy (FTIR). The oil and grease concentration was determined according to standard method from the department of environmental. A result of the experiments shows that the highest DDA (79.55%) is from chitosan treated in 50% NaOH at 90^{o}C for 5 hour. Using this chitosan, 99.30% oil and grease concentration is removed from the POME wastewater. In conclusion, the highest DDA is obtained by treating chitin with 50% NaOH at 90^{o}C for 5 hour (Chinadit *et al.,* 1998) and by using this chitosan maximum O&G is removed from POME wastewater.

ABSTRAK

Tesis ini adalah mengenai rawatan bahan buangan minyak sawit (POME) dengan menggunakan chitosan dan darjah diasitilasi (DDA) akan dikaji. Chitosan dikenali sebagai chitin yang diasitilasi atau lebih dikenali sebagai salah satu bahan di dalam produk menguruskan badan kerana sifatnya yang boleh menyerap minyak dan dengan sebab inilah ia sesuai digunakan dalam merawat POME. Salah satu kaedah yang digunakan untuk merawat bahan buangan minyak sawit ialah dengan menggunakan teknologi membran. Kaedah ini walaupun mempunyai kadar pemisahan yang tinggi, memerlukan banyak proses dan melibatkan kos yang tinggi. Oleh itu, kajian tentang kesan DDA keatas POME patut dijalankan. Peratusan molar natrium hidroksida (NaOH), suhu dan masa rawatan ke atas chitin diubah di dalam lingkungan 30 hingga 70% NaOH, 40 hingga 90^{o}C dan 5 jam hingga 3 hari. Chitin akan direndam didalam kaedah rawatan yang berbeza. DDA akan dikira berdasarkan nilai absorban yang diperoleh daripada graf yang didapati daripada spektroskopi perubahan infra merah Fourier (FTIR). Kandungan minyak (O&G) yang dipisahkan daripada POME juga dikira dengan menggunakan kaedah yang telah ditetapkan oleh jabatan alam sekitar. Keputusan eksperimen menunjukkan nilai DDA tertinggi yang diperoleh ialah 79.55% iaitu pada kaedah rawatan 50% NaOH pada suhu 90^{o}C untuk 5 jam dan apabila chitosan ini digunakan untuk merawat POME sebanyak 99.30% kandungan minyak (O&G) dapat dibuang. Kesimpulannya, DDA tertinggi dalam eksperimen diperoleh dari kaedah rawatan 50% NaOH pada suhu 90^{o}C untuk 5 jam selaras dengan penyelidik sebelum ini yang menyimpulkan bahawa DDA tertinggi boleh diperoleh pada kaedah rawatan yang dinyatakan dan apabila chitosan ini digunakan ia dapat menyingkirkan kandungan minyak (O&G) yang paling maksimum.

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LIST OF ABBREVIATIONS

DDA	Degree of Deacetylation
FTIR	Fourier Transform Infrared Spectroscopy
HPLC	High Performance Liquid Chromatography
H-NMR	H-Nuclear Magnetic Resonance Spectroscopy
NaOH	Sodium Hydroxide
UMP	University Malaysia Pahang
HCl	Hydrochloric Acid
NaOCl	Sodium Hypochloride
H_2SO_4	Sulphuric Acid
O&G	Oil & Grease
POME	Palm Oil Mill Effluent
U.S.A	United State of America
IR	Infrared
KBr	Potassium Bromide
CPO	Crude Palm Oil
GHG	Green House Gases
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
TS	Total Solids
SS	Suspended Solids
TVS	Total Volatile Solids
AN	Ammoniacal Nitrogen
TN	Total Nitrogen
^{o}C	Degree Celcius
%	Percent
$\geq$	Same or More Than
$<$	Less Than

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Few decades ago, shrimp shells are considered a waste because people usually use the shrimp itself without its shell. But, time has change and shrimp shells are now considered important as a raw material for chitosan production because of its composition of long chain polymer polysaccharide beta-glucose, a type of natural polymer.

Basically, chitosan is very famous as one of the main ingredient in slimming product because of its ability to absorb oil. Today there is growing interest in chitosan because of its usefulness in many fields from food industry to oily wastewater treatment. Nowadays, this compound is attracting widespread interest in the industry that produces oily wastewater because of its ability to grab oil from the wastewater without adding any other chemical compound.

The use of chitosan in treating oily wastewater can help produce cleaner wastewater to be release to the river. A few treatment of wastewater has proved that chitosan can really help in separating compound such as heavy metal from wastewater. However, it is not known at what degree of deacetylation it is that the chitosan can absorp most oil from the wastewater. Today this matter can be handled by modifying the chitin used to produce chitosan by varying the degree of deacetylation. The analytical equipment used is Fourier Transform Infrared Spectroscopy (FTIR).

In the near future, there will be more and more application of chitosan especially in the treatment of oily wastewater. Therefore, it is crucial that the degree of deacetylation that can separate oil the most from the oily wastewater is researched. As a matter of fact this paper presents a research to study the best degree of deacetylation to separate the oil from the oily wastewater. It is best to study the degree of deacetylation because it is the main factor that can affect the ability of a certain chitosan.

1.2 Problem Statement

For the past few years, researchers have done many researches on chitin and chitosan for its use in many industries and it has been proven effective to remove acid dyes from textiles wastewater, remove metal ions from wastewater, remove heavy metal from industrial wastewater and as an additive to thicken and stabilize foods and pharmaceuticals (Wikipedia Website). There are also researches on the degree of deacetylation (DDA) of chitosan for example Lertsutthiwong *et al.*, 2002 concluded in his report that different chemical treatments in the production of chitin and chitosan result in variation in the characteristics (viscosity, DDA, moisture and ash content) of chitosan. However, there are no specific researches on the degree of deacetylation (DDA) of chitosan that can remove oil from the wastewater most effectively. As a concern of this matter, this study is conducted based on the potential of chitosan itself to separate oil from wastewater effectively. The equipment used in determining the DDA of the chitosan is Fourier Transform Infrared Spectroscopy (FTIR). The sample palm oil mill effluent (POME) wastewater used is from Felda Lepar Hilir. POME wastewater can be treated using membrane technology but it require a lot of process and there will also be problem with maintenance and fouling which will increase overall cost of the plant. This is quite expensive compared to the use of chitosan itself to react with POME wastewater that will be cheaper without the cost on maintenance. Now, the only thing needed is the degree that can remove the most oil content from the POME wastewater. This is where this study comes in, because there is in fact no study has been recorded on the degree of deacetylation that can absorb oil the most from POME.

1.3 Objective

The main objective of the research is to study the effect of varying the degree of deacetylation of chitosan (DDA) in treatment of palm oil mill effluent (POME) wastewater.

1.4 Scope of Research

Chitin is transform into chitosan with different degree of deacetylation by varying

- Molar percentage of sodium hydroxide added to the chitin (30 to 70%)
- The temperature of the process (40^{o}C to 90^{o}C)
- The time range of the process (5 hr to 3 days)

The chitosan is used to treat palm oil mill effluent (POME) wastewater collected from Lepar Hilir.

CHAPTER 2

LITERATURE REVIEW

2.1 Shrimp Shell

Shrimp is the first of the top ten foods exported in the year 2000 by Thailand with a 15% export share (National Food Institute, 2001). It is exported fresh, chilled, frozen, boiled and frozen-dried or salted in brine and as a value-added product. The major markets for frozen shrimps are the U.S.A., Japan and Singapore (Department of Business and Economics, 1999). Shrimp industries generate large amounts of shrimp biowaste during processing, approximately 45-55% of the weight of raw shrimp. The waste is sold to feed mills at a low price. However, this biowaste can be used to produce value-added products because it is rich in protein, carotenoids and chitin. Shown in Figure 2.1 is shrimp shell used in production of chitosan.

Figure 2.1 Shrimp shell

2.2 Chitin

Currently, nearly all chitin and chitosan produced commercially are chemically extracted from crab, shrimp and prawn exoskeleton waste (Roberts, 1997). Chitin can also be produced from shell waste by fermentation with microorganisms or with the aid of enzymes (Rao, *et al.*, 2000). Enzymatic deacetylation of chitin to chitosan has been accomplished at the lab scale, but is not yet available for industrial scale (Win, *et al.,* 2000; Win, *et al.,* 2001). The chemical extraction of chitin is based on demineralization (or decalcification) by acid and deproteination by the action of alkali. Chitin is deacetylated into chitosan in concentrated alkaline (Roberts, 1997).

Chitin is a polymer composed of D-glucopyranose units with an N-acetylamino group at the C2 position of the glucopyranosyl ring. It can be found in anything from the shells of beetles to the webs of spiders (Sacha, 2004).

Chitin is a cellulose-like biopolymer consisting of unbranched chains of predominantly β-(1 $\rightarrow$ 4)-2-acetamido-2-deoxy-D-glucose (also named N-acetyl-D-glucosamine) residues. The structure of chitin is shown in Figure 2.2. It does not dissolve in standard polar and non-polar solvents. It is present in fungi, yeast, marine invertebrates and arthropods, where it is a principal component in the exoskeleton (Jeuniaux, 1996).

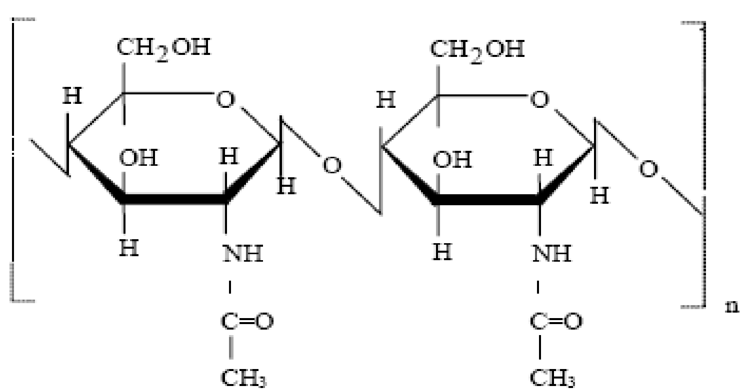

Figure 2.2 Structure of chitin

The difference between chitin and cellulose is that cellulose contains a hydroxy group, while chitin contains acetamide. When applied to human wounds and surgical cloths, it accelerates the skin healing process. An acidic mixture of chitin, when applied to burns, also accelerates the healing process. Left on for a few days, it can heal a third-degree burn completely (Sacha, 2004).

Chitin is used industrially in many processes. It is used in water purification, and as an additive to thicken and stabilize foods and pharmaceuticals. It also acts as a binder in dyes, fabrics and adhesives. Industrial separation membranes and ion-exchange resins can be made from chitin. Processes to size and strengthen paper employ chitin. Most recent studies pointed out that chitin are a good inductor for defense mechanisms in plants. It was recently tested as a fertilizer that can help plants develop healthy immune responses, and have a much better yield and life expentancy (Wikipedia Website).

2.3 Chitosan

Chitosan is a linear polysaccharide composed of randomly distributed β-(1-4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit). The structure of chitosan is shown in Figure 2.3 and 2.4. It is produced commercially by deacetylation of chitin, which is the structural element in exoskeleton of crustaceans (origin from crabs, shrimp, etc) (Shahidi and Synowiecki, 1991). The amino group in chitosan gives a pKa value of ~6.5. Thus, chitosan is positively charged (cationic) and soluble in acidic to neutral solution with a charge density dependent on pH and the %DA-value. Besides, chitosan is bioadhesive and readily binds to negatively charge surfaces such as mucosal membranes.

Purified chitosan is commercially used in the biomedical applications. It is because chitosan enhances the transport of polar drugs across epithelial surfaces, besides its nature of biocompatible and biodegradable (Shahidi and Synowiecki, 1991).

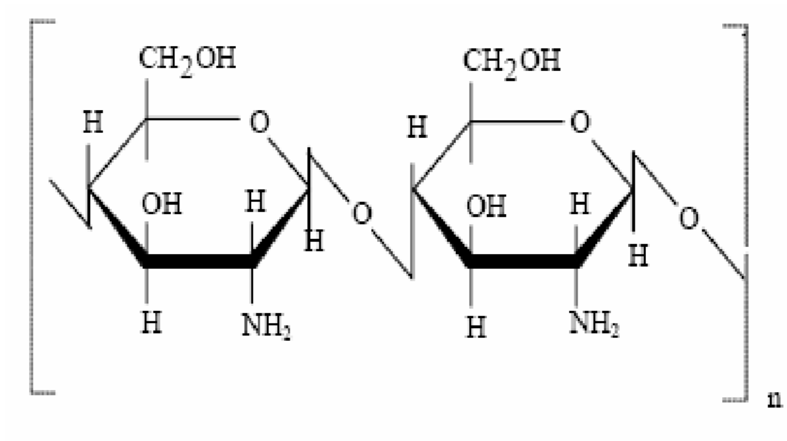

Figure 2.3 Structure of chitosan

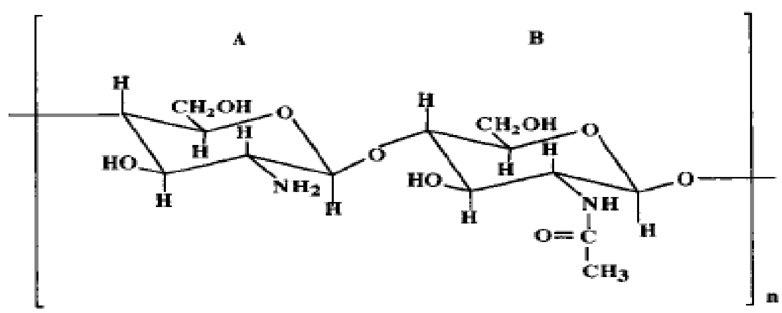

Figure 2.4 Chitosan ≥ 75% A (β-D-glucosamine) and < 25% B (N-acetyl- β-D-glucosamine) with n approximately 1000.

Chitosan and its derivatives such as trimethylchitosan are also have been used in non-viral gene delivery. Trimethylchitosan, or quaternised chitosan, has been shown to transfect breast cells. With increased degree of trimethylchitosan, it increases the cytotoxicity and at approximately 50% trimethylation the derivative is the most efficient at gene delivery. Oligomeric derivatives (3-6 kDa) are relatively non-toxic and have good gene delivery properties (Kean *et. al.,* 2005).

Chitosan is also used primarily as a plant growth enhancer, and as a substance that boosts the ability of plants to defend against fungal infections. It is approved for use outdoors and indoors on many plants grown commercially and by consumers.