

DEVELOPMENT OF EMULSIFIED WASTEWATER TREATMENT SYSTEM

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DEVELOPMENT OF EMULSIFIED WASTEWATER TREATMENT SYSTEM

CHONG HON YVAIN

Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering

**Faculty of Chemical & Natural Resources Engineering
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JANUARY 2014

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Dedication

In memory of my grandmother, Seow Ah Mooi,
For the fearlessness to finish this dissertation

&

To my family, with my deep love, appreciation
and hope for a better future

Chong Kok Leong
Sujata Tan Kim Suan
Metta & Mitra

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ABSTRACT

Emulsions are commonly used in metal processing productions as emulsified coolant and lubricating oil. These emulsions will be discharged off as emulsion waste after losing their efficiency. These wastes have to be treated to satisfy the standard limits before being discharged to waterways to prevent pollutions. This work targets to develop an emulsified wastewater treatment system using effective bio-coagulant and low cost agricultural waste as bio-adsorbent. Chitosan and rubber seed shell activated carbon (RSSAC) as bio-coagulant and bio-adsorbent respectively will be employed in this work. Samples of emulsified wastewater were collected and analysis was done. Activation of chitosan powder was prepared by diluting it with acetic acid and distilled water. The fresh rubber seed was cracked to get the shell which was then washed, sun-dried, pulverised and sieved and impregnated with NaOH before carbonization to produce RSSAC. Carbonization was able to increase the S_{BET} up to 20 folds. Results show the highest reading of S_{BET} ($19.2403\text{m}^2/\text{g}$) at 650°C compared to S_{BET} ($0.9482\text{m}^2/\text{g}$) before carbonization. Carbonization is able to remove volatile compounds and promotes formation of new pores. However, the S_{BET} dropped at high temperature 850°C because of surface erosion and rupture of some porous wall which causes lower porosity formation. Jar test method was used with chitosan as coagulant at primary treatment followed by RSSAC as adsorbent at secondary treatment. Effects on removal of oil & grease (O&G), total suspended solids (TSS), turbidity and pH value were studied in this paper by varying the contact time and dosage. The combined system able to reduce 90% of O&G compared to chitosan alone which only able to reduce up to 76%. The chitosan able to agglomerate and demulsify emulsion and improve the residual oil coagulation. Further addition of RSSAC able to adsorb the remaining oil left from the primary treatment. The treatment is able to reduce TSS and turbidity up to 98.7% and 92.5% respectively. Treated wastewater can be further processed by using membrane ultrafiltration to remove residual RSSAC. Also, the colour indicates the presence of heavy metals and can be further treated to improve filtrate clarity. RSS may be further explored into producing activated carbon by other means of activation and used adsorb other types of substance such as dyes, heavy metals and other impurities. Present work is able to treat emulsion waste by using effective bio-coagulant and low cost industrial waste as bio-adsorbent.

ABSTRAK

Emulsi lazimnya digunakan dalam industri pemrosesan logam sebagai bahan penyejuk dan minyak pelincir. Sisa emulsi akan dibuang selepas digunakan. Sisa ini perlu dirawat bagi memenuhi had standard sebelum dilepaskan ke laluan air untuk mengelakkan pencemaran. Objektif kerja ini adalah untuk menstrukturkan satu sistem rawatan air sisa emulsi dengan menggunakan bio-koagulan berkesan dan kos rendah sisa pertanian sebagai bio-penjerap. *Chitosan* dan kulit biji getah sebagai bio-koagulan dan bio-penjerap akan digunakan dalam eksperimen ini. Sampel air sisa emulsi dikumpulkan dan analisis telah dijalankan. Pengaktifan serbuk chitosan telah disediakan dengan melarutkan ia dengan asid asetik dan air suling. Benih getah segar telah diretak untuk mendapatkan kulit dan kemudiannya dibasuh, dikering, dikisar, diayak dan diaktifkan dengan NaOH sebelum proses karbonisasi untuk menghasilkan RSSAC. Karbonisasi dapat meningkatkan S_{BET} sehingga 20 kali ganda. Keputusan menunjukkan bacaan tertinggi $S_{BET}(19.2403\text{m}^2/\text{g})$ pada 650°C berbanding $S_{BET}(0.9482\text{ m}^2/\text{g})$ sebelum proses karbonisasi. Karbonisasi berkesan untuk menggalakkan pembentukan liang baru. Walau bagaimanapun, nilai S_{BET} menurun pada suhu 850°C adalah kerana hakisan permukaan dinding berliang. *Jar-test* telah digunakan dengan *chitosan* sebagai koagulan di rawatan utama diikuti dengan RSSAC sebagai penjerap pada rawatan selanjutnya. Kesan ke atas pengurangan *O&G*, *TSS*, *turbidity* dan pH dikaji dalam kertas ini dengan mengubah masa dan dos. Sistem *chitosan* + RSSAC dapat mengurangkan 90% *O&G* berbanding dengan *chitosan* sahaja yang hanya dapat mengurangkan sehingga 76%. *Chitosan* menggumpal dan meningkatkan pengumpulan sisa minyak dari emulsi. RSSAC pula dapat menjerap minyak yang tertinggal daripada rawatan pertama. Rawatan ini dapat mengurangkan *TSS* dan *turbidity* sehingga kepada 98.7 % dan 92.5 %. Air sisa yang telah dirawat boleh diproses dengan lebih lanjut dengan menggunakan *ultrafiltration membrane* untuk memerangkap sisa RSSAC. Selain itu, warna yang menunjukkan kehadiran logam berat boleh dirawat dengan lebih lanjut untuk memperbaiki kejelasan hasil turasan. RSS boleh terus diterokai untuk menghasilkan karbon dengan cara-cara lain pengaktifan dan digunakan untuk menjerap jenis bahan-bahan lain seperti pewarna, logam berat dan kekotoran lain. Kajian ini mampu merawat sisa emulsi dengan menggunakan bio-koagulan berkesan dan sisa industri kos rendah sebagai bio-penjerap.

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LIST OF ABBREVIATIONS

BOD	Biochemical oxygen demand
CAC	Commercial activated carbon
CNC	Computer numerical control machine
COD	Chemical oxygen demand
DOE	Design of experiment
GAC	Granular activated carbon
MTZ	Mass transfer zone
NOM	Natural organic matter
O&G	Oil and grease
O/W	Oil in water
PAC	Powdered activated carbon
RSCC	Rubber seed coat carbon
RSS	Rubber seed shell
RSSAC	Rubber seed shell activated carbon
SCD	Streaming current detector
TSS	Total suspended solids
W/O	Water in oil

1.0 INTRODUCTION

1.1 Motivation and brief review

This research will be conducted to evaluate the coagulation and adsorption performance of chitosan and rubber seed shell activated carbon (RSSAC) in emulsified wastewater respectively. The effects of various process variables in this research will be reviewed.

Chiefly, water is a basic source of life, energy and is a fundamental for human consumption, agricultural process, economic activity and an important part in the ecosystem. As rapid industrialization and economic expansion, unseen constraints on freshwater resources are growing and caught the public's attention on the limits to water availability. Many places are expecting the point of peak water and there is a need to shift the way of management of freshwater resources towards a more productive, efficient and ecological use (Gleick & Palaniappan, 2010). Management in water works have been explored and expanded to support water demand. Type of facilities such as large dams, treatment plants, wells and pipelines are constructed according to characteristics and life expectancy for continuous water supply to houses, commercial and institutional facilities (Davis, 2010).

Surface water and ground water are the two basic fresh water supplies. Surface waters are the ones which are highly exposed to hazardous waste and toxic effluents. Though a fraction of the United States populations are supplied with groundwater, but it do have its cons. Groundwater contains minerals which may cause unwanted characteristics such as hardness, color from iron oxidation and arsenic from beneath the earth's surface (Davis, 2010). In addition to that, groundwater is estimated about only 0.61% of the world's water which is very limited ("Columbia Water Center", 2013). This is why surface water is to be managed wisely. With the ongoing rise of water supply risk, climate variability and pollution from industrial activities into surface waters, this proves the urgency to protect and manage surface water in a long term perspective.

Generally, global population is foreseen to hit up soon. Meaning that more usage and demand of water in the future. The chief source of freshwater pollution is due to untreated effluents and toxic industrial wastes. It is proven that water contaminations which causes up to 70-80% of illness in developing countries are from pollution discharge. It also causes a negative impact on aquatic life and the balance of the ecosystem (“Global Water Supply and Sanitation Assessment Report”, 2000). The environmental issues caused by modern industrial technologies especially in the discharging of untreated effluents leads to scheduled wastes which is a material that contains chemicals exceeding the threshold amount and the parameters limits of discharge quality, Standard A and B as stated in the Environmental Quality Act 1974. It is a crucial element to make sure that any effluents or discharges of water have to be under all the parameter limits before is it allowed to be released into waterways. Figure 1-1 below shows the acceptable limits of the parameter of effluents under the Standard A and B.

THIRD SCHEDULE
ENVIRONMENTAL QUALITY ACT 1974
ENVIRONMENTAL QUALITY (SEWAGE AND INDUSTRIAL EFFLUENTS)
REGULATIONS 1979
(REGULATIONS 8(1), 8(2), 8(3))
PARAMETER LIMITS OF EFFLUENTS OF STANDARDS A AND B

Parameter	Unit	Standard	
		A	B
(i) Temperature	°C	40	40
(ii) pH value	-	6.0 - 9.0	5.5 - 9.0
(iii) BOD at 20°C	mg/ l	20	50
(iv) COD	mg/ l	50	100
(v) Suspended Solids	mg/ l	50	100
(vi) Mercury	mg/ l	0.005	0.05
(vii) Cadmium	mg/ l	0.01	0.02
(viii) Chromium, Hexavalent	mg/ l	0.05	0.05
(ix) Arsenic	mg/ l	0.05	0.10
(x) Cyanide	mg/ l	0.05	0.10
(xi) Lead	mg/ l	0.10	0.5
(xii) Chromium Trivalent	mg/ l	0.20	1.0
(xiii) Copper	mg/ l	0.20	1.0
(xiv) Manganese	mg/ l	0.20	1.0
(xv) Nickel	mg/ l	0.20	1.0
(xvi) Tin	mg/ l	0.20	1.0
(xvii) Zinc	mg/ l	2.0	2.0
(xviii) Boron	mg/ l	1.0	4.0
(xix) Iron (Fe)	mg/ l	1.0	5.0
(xx) Phenol	mg/ l	0.001	1.0
(xxi) Free Chlorine	mg/ l	1.0	2.0
(xxii) Sulphide	mg/ l	0.50	0.50
(xxiii) Oil and Grease	mg/ l	Not Detectable	10.0

Figure 1 - 1 : Parameter limits of effluent of Standards A and B. Adapted from “Environmental Quality (Sewage and Industrial Effluents) Regulations 1979”, p. 107

Standard A is a more stringent guide because Standard A is applied as a regulation at the water catchment areas which includes areas upstream of surface or above sub-surface of waterways, mainly directed to the community and for human use. On the other hand, Standard B applies to effluent that leads to the downstream waterways such as the sea (“Environmental Quality: Sewage and Industrial Effluents Regulations”, 1979). BOD, COD and TSS limits are all below 100mg/L for both standards. Mercury and phenol are having the least allowable limit of 0.005mg/L and 0.001mg/L respectively. Chromium-trivalent, copper, manganese, nickel, tin and zinc are to be less than 1.0mg/L for both standards. Arsenic and cyanide have to be less than 0.1mg/L. Boron and iron each have to be less than 4.0mg/L and 5.0mg/L respectively. Oil and grease, the most significant parameter in this research is to be under 10.0mg/L for standard B.

On the other hand, emulsified wastewaters are one of the major toxic wastes from the metal processing industry. Oil in water (O/W) is a type of emulsions where it is a hydrophobic solvent which dispersed in an aqueous medium (“Pollution Prevention Guidance Manual for the PFPR Industry”, 1998). Emulsions are commonly used in metal processing productions as emulsified coolant and also in power plant as lubricating oil. They are also commonly referred as cutting fluid, cutting oil, coolant or lubricant. Usually after they lost their efficiency, these emulsion waste will be discharged off or sent for treatment. On top of that, there are emulsion wastes being produced monthly in a common mechanical lab or plant. Used oils must be reused or have proper disposal methods by local waste management authorities or automotive plant. It is because engine lubrication oil, gear oils or machine oils are a major source of oil contamination of waterways. These emulsions are insoluble and are exposed to toxic chemicals and heavy metals (“Used Oil Management Program”, 2012).

Majority of the industrial waste in Malaysia is sent to Kualiti Alam Sdn. Bhd. for treatment and disposal periodically. Referring to Kualiti Alam Sdn Bhd’s treatment rates for scheduled waste, it is very costly and used up a lot of resources especially in transportation and treatment. Therefore, it is ideal in the present to develop an emulsified wastewater treatment system. Breakthroughs on technologies on water treatment have been developed over the years and chemical treatment is one

of the most useful and utilized techniques in wastewater treatment process (Sharma & Sanghi, 2012). Chemical treatment usually involves coagulation and flocculation process as a primary treatment then followed by secondary stage (Sharma & Sanghi, 2012). Among secondary stage are filtration, foam flotation, ion exchange, aerobic and anaerobic treatment, electrolysis, solvent extraction and adsorption. Adsorption is considered as an ideal treatment due to the process's fundamental design and direct procedures (Bhatnagar & Sillanpaa, 2010). Physical adsorption method will be employed in this study by using natural bio-sorbent, chitosan. The work is also extended to study the chelation behavior of RSSAC.

1.2 Problem Statement

It is costly to frequently send out emulsion waste for treatment. From a conducted survey, it was estimated that a manufacturing plant will produce around 20 tonnes of wastewater every month. Meaning that, 240 tonnes of wastewater is produced every year. This scheduled wastewater is disposed to Kualiti Alam Sdn. Bhd. at a rate of RM 3000.00 per tonne. Hence, each plant will spend more than RM 720,000.00 per year. In Malaysia, there are more than 100 manufacturing plant and are still counting. Therefore, RM72 million per year will be the total spending to treat them. Since lots of money being spent by the industry to dispose the waste water, it is rational to conduct a research to tackle this matter.

Therefore, it is feasible to have a treatment facility which runs on affordable budget yet having high performance emulsion breaking system. Despite having potential in improving adsorption methods in treating wastewater, there are only a handful of studies that have focused on using biomaterials as adsorbent. A cheaper alternative in adsorbent is also a more feasible factor in terms of economic production. In this work, biomaterials chitosan and RSSAC will be used.

1.3 Research Objective

This work targets to develop an emulsified wastewater treatment system

1.4 Research Scope

- To do a characterization study on the wastewater sample to act as a reference material for after treatment
- To construct an experiment to study the adsorption/flocculation performance of chitosan with respect to its concentration/dosage and mixing time
- To construct an experiment to study the adsorption performance of RSSAC
- To conduct characterization study on treated sample
- To reduce the pH, TSS, O&G and Turbidity level under the acceptable limits of the Standard A and B water quality
- To compare the performance of chitosan and RSSAC in demulsification

2.0 LITERATURE REVIEW

2.1 Chapter Overview

Being the utmost importance of wastewater treatment technologies and design, the need of its quality breakthroughs, improvements and preservation are growing continuously. Two treatment methods, coagulation and adsorption will be used for chitosan and RSSAC respectively in this research. Adsorption and coagulation technology including theories, type of adsorbents and coagulants and findings will be reviewed in this chapter. Characteristics of emulsified wastewater used in this research will also be discussed. Fundamentals theories of adsorption equilibria such as Langmuir and Freundlich isotherm will not be discussed in this particular research. This exploratory research will be focusing on the adsorption performance of bio-sorbents rather than constructing an adsorption isotherm or determining the maximum or ultimate capacity.

2.2 Emulsion

Generally, emulsions contain three basic components which are oil, some emulsifying agent and water. Emulsifying agent will form a layer boundary around the oil droplet which made the oil droplet suspended in the water. The breaking of emulsion layer is the target way of treating this particular waste. Breaking of emulsion is also known as demulsification. Demulsification is the utmost important processes in metallurgical, food and chemical industries, where they frequently generate a large quantity of water-in-oil (W/O) and (O/W) liquid waste (Kukizaki & Goto, 2008).

To date, many methods for demulsification have been practiced such as electrical, temperature change, distillation, centrifuging, ultrasonic vibration, agitation and filtration but all these are mostly shifted out due to the economic and convenience reason and are not been explored thoroughly (Milne, 1950). Although membrane demulsification is proven to have high efficiency, but it has energy costs and is a complex process (Kukizaki & Goto, 2008). On top of that, although chemical breaking methods by reacting emulsifying agent with salts of polyvalent metals are

satisfactory, but they use large quantity of chemicals and are not environment friendly (Milne, 1950).

Raw emulsified wastewater will be used in this exploratory research. A summary of the emulsified wastewater from a metallic processing machine parameter results are as shown below.

Table 2 - 1 : Parameter values of the raw emulsified wastewater.

No	Parameter	Results	Unit
1	Density	1.001	g/cm ³
2	Turbidity	70	NTU
3	pH	9.71 @ 24.5°C	-
4	TSS	More Than 750	mg/L
5	O&G	More Than 100	mg/L
6	Viscosity	132.6	cP

Theses analyzed values are way above the acceptable limits set as shown in Figure 1-1 previously. The reported results of turbidity, TSS and O&G are all at risk which proves that the waste is hazardous and is not ready to be discharged into the waterways.

2.3 Treatment Method: Coagulation and Flocculation

Coagulation and flocculation are ideal elements in conventional water treatment because they are capable in

- Preventing the formation of disinfection byproducts
- Removing disease spreading particles
- Removing toxic substance that have adsorbed to the surface of particles
- Treat the water to a suitable standard (Davis, 2010).

Chemical water treatment usually involves coagulation and flocculation process as a primary treatment then followed by secondary stage (Sharma & Sanghi, 2012). Coagulation and flocculation are pretreatment processes and they only assist in their efficiency of removal in further separation operations and do not remove contaminants (Edzwald, 2011) Coagulation is a complex process where it improves the ability of small particles in an aqueous suspension to attract among itself and to adsorbents (Edzwald, 2011). In addition, the purpose of coagulation is to transform the small particles into larger particles called flocs. Flocs are usually formed as precipitates or as suspended materials. They are readily to be removed easily via settling, dissolved air flotation or filtration (Davis, 2010). There are four basic mechanisms in chemical coagulation, namely

- a) Ionic layer compression,
- b) Charge neutralization,
- c) Entrapment in a flocculent mass and interparticle bridging (Peavy, et al., 1985).

The last mechanism, the physical interparticle bridging is termed flocculation (Edzwald, 2011). Flocculation leads to floc formation by slow mixing. It does not only increase the size of particle but it also affects the physical nature of the floc. Flocs are of different sizes which lead to the reason why they have different settling rates. Settling velocities causes the particles to interact and form flocs.

a) Ionic Layer Compression (Compression of the electric double layer)

The effectiveness of coagulation is to reduce the repulsion forces between two meeting particles when are brought together so that the adsorbate could easily attach itself to the adsorbent. When the electric double layer is compressed, the repulsive force will be lesser and encourages the formation of flocs by the nature of Brownian motion and van der Waals forces of attraction. The stronger the compression, a more rapid flocculation will occur.

b) Charge Neutralization

Hydrolyzed metal salts, prehydrolyzed metal salts and cationic polymers possess a positive charge. They destabilize particles through charge neutralization.

c) Entrapment and interparticle bridging

Polymer chains adsorb on particle surfaces at one or more than one site. The remaining empty sites on the polymer chain tend of extend into solution and adsorb on another neighboring particle which forms a connection between the particles. These connections then extend and eventually form a large particle which are able to settle more efficiently and a denser compound. With doses above the saturation level for coagulation, the coagulant will then form insoluble precipitates and particulate matter is entrapped in the precipitate (Davis, 2010).

In order to understand better in this mechanics, jar test experiment to determine the coagulant dosage are advisable instead of formula calculation of the theory. Chemistry of coagulation is intensely complex (Davis, 2010). Laboratory Jar test is an ideal way in illustrating the mechanics of coagulation. On the other hand, flocculation depends on the turbulence and duration of mixing and is the interaction between

destabilized particles and between particles and flocs which will be reviewed as well (Peavy, et al., 1985).

2.3.1 Mixing Theory

High velocity gradients are ideal for coagulation. Flocculation needs a very high velocity to improve the particle interaction at the same time prevent settling of particles at the beginning (Crittenden & Thomas, 1998). The speed must be lowered at a later stage to prevent the flocs from disintegrating which will lead to tearing apart. Flocculation mixing time at later stage is more dependent in the study. As discussed by Davis (2010), conventional treatment flocculation time ranges from 20 to 30 minutes for settling because it will affect the degree of reaction completion. Mechanical mixing in stirred tanks will be employed in the study through the Jar Test.

2.3.2 Coagulant Aids

Coagulant aids are included to improve the floc settling time because their density is higher than most floc particles formed from the beginning. They are commonly used in waters that possess low concentration of particles and also waters that have few nucleating sites to form large flocs (Davis, 2010). Clay, sodium silica and activated carbon are among commonly used aids to improve turbidity in water.

2.3.3 Coagulant Selection

2.3.3.1 Inorganic Coagulant

These materials can be segmented into inorganic coagulant and synthetic organic polymers. They are being widely used in the water treatment industry mainly to remove turbidity and other hazardous substances. The disadvantages in using these chemical based coagulants are as follows:

- Affect pH of water after treatment
- Ineffective in low-temperature water
- High procurement costs
- Negative effects on human health
- High quantity of sludge produced (Yin, 2010).

Despite being cheap and known to be the most widely used coagulants in water and wastewater treatment in the world, the presence of residuals after treatment are unwholesome and undesirable due to their neurotoxicity and heavy carcinogenic characteristics which are unsafe for human health (Mallevialle et al., 1984). With a large amount of these coagulant used, therefore generating a large quantities of sludge.

Coagulant recovery from water treatment works are being practiced since back at the year 1970's but was discontinued due to lack of literature and specifications (Keeley et al., 2011). If coagulant recovery or recycling can be done, then this would save up coagulant cost and thus providing a higher efficiency treatment process. However, this situation has been overruled by the present high treatment efficiency. Members of the public are focusing on the treatment of waste but are not mindful on the economic and environmental consequences of post treatment. There are hardly any published literatures on inorganic coagulant recovery after treatment. Examples of inorganic and synthetic organic polymers coagulant are as follows.

a) Metal Salts

Alum, ferric chloride and ferric sulfate are the most common coagulants. These metal salts are very robust over a wide range of variable pH. These metal salts hydrolysis products react with F^- , SO_4^{2-} , PO_4^{3-} and natural organic matter (NOM), and form soluble and insoluble particles (Davis, 2010). The usual concentrations of alum are from 10 to 150mg/L, ferric chloride from 5 to 150mg/L and ferric sulphate from 10 to 250mg/L. They are among the best in NOM removal provided is done with the right dosage and selection of coagulant.

b) Polymer

Polymers are a promising coagulant in the strength to reduce metal salt concentration and producing sludge production up to a high 80%. Generally, polymers are known to be slightly affected by pH and the usual dosages are from only 1 to 10mg/L. On the other side, polymers are ineffective in NOM removal (Davis, 2010).

2.3.3.2 Natural Coagulant

In comparison to inorganic coagulants, natural coagulants are produced or extracted from microorganisms, plant or animal tissues. These natural coagulant or also known as bio-coagulants are biodegradable, non-toxic and safe for human (Kumar, 2000). Being biodegradable, it produces less amount of volume of sludge that consists only 20-30% that of alum treated otherwise (Sciban et al., 2009). On top of that, it is obviously cost effective since its productions are mainly from agricultural waste and other renewable resources. It is also rarely will produce treated water with extreme pH value (Yin, 2010). Chitosan, a component from the exoskeleton of sea material will be employed in this research and will be discussed in the following section of this literature review.

2.3.4 Chitosan as Coagulant

Chitosan is a modified, natural and a versatile biopolymer derivative that is produced by alkaline deacetylation of chitin which is a component of the exoskeleton of crustaceans such as lobster, prawn, crab (Kim, 2011). It is nontoxic, antiviral, antifungal, biodegradable, biocompatible, and has flocculating ability. Chitin is composed of β (1 \rightarrow 4)-lined 2-acetamido-2-deoxy- β -D-glucose (N-acetylglucosamine). It can be related as cellulose with a hydroxyl at position C-2 replaced by an acetamido group. Chitosan is the N-deacetylated derivative of chitin (Kumar, 2000). Agricultural materials especially those possesses cellulose shows

potential sorption capacity for a variety of pollutants (Bhatnagar & Sillanpaa, 2010). Cellulose, chitin and chitosan all acts naturally as a structural polysaccharide which is a better alternative to the synthetic polymer materials. The latter two are of industry interest because of their nitrogen percentage of 6.89% compared to cellulose of 1.25% which made them a better chelating species (Muzzarelli, 1973). The structures of cellulose, chitin and chitosan are shown in Figure 2-1.

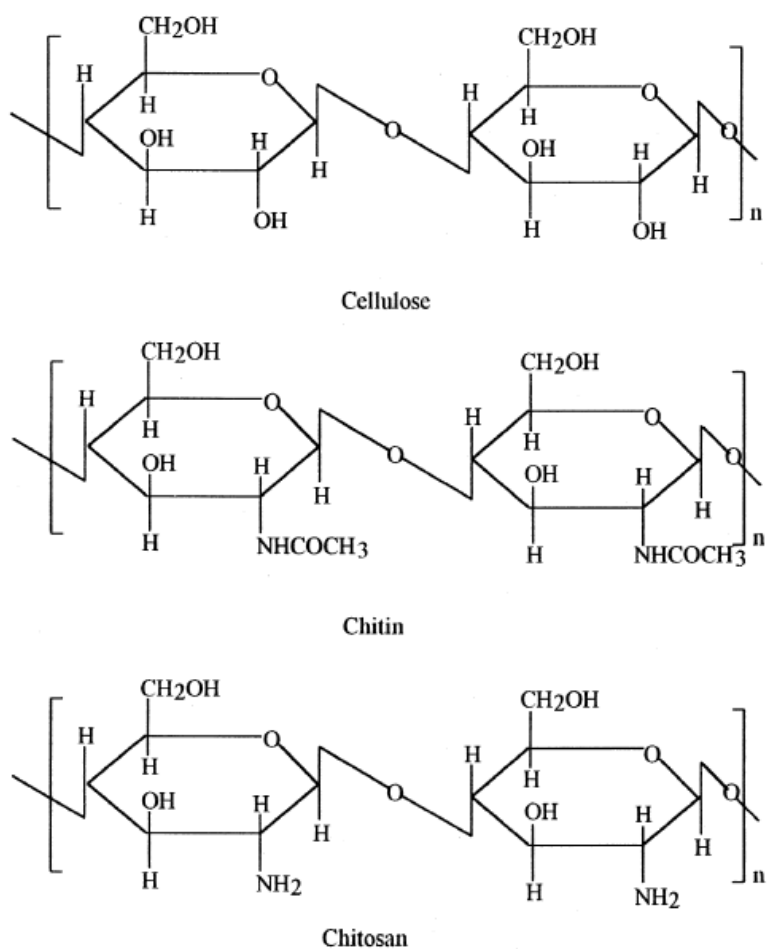


Figure 2 - 1 : Structures of cellulose, chitin and chitosan. Adapted from “A Review of Chitin and Chitosan Application” by M.N.V.R. Kumar, 2000, *Reactive & Functional Polymers*, 46, p.1-27.

Chitosan has tremendous contribution in various industries from drug delivery in medical, beverage, cosmeticceuticals to food industry and there are hardly any published articles on chitosan’s ideal ability in emulsified wastewater treatment. Since it’s a global interest on the use of renewable resources in industry and is a very abundant material, chitosan seems like a prominent choice as a bio adsorbent (Kim,

2011). Fisheries wastes such as crab shells and prawn from Asian countries including Thailand, Japan and China are being focused to be developed into chitosan. Raw materials can be obtained for free from the local fishermen (Ahmaruzzaman, 2008). Studies showed chitosan's ability in dye removal, coagulation and flocculation as well as a heavy metal removal especially for copper (Kim, 2011). Chitosan molecules are also known in removing heavy metals and oils from water. Higher molecular weight and higher degree of deacetylation of chitosan powder have properties that show stronger adsorption strength compared with its opposite counterpart. The prolonged adsorption process is due to the constant disentanglement of the polymer molecules (Chattopadhyay & Inamdar, 2010).

Activation of chitosan will be done by coagulating the chitosan powder with dilute acids to form a gel for treatment purposes. Chitosan is soluble in dilute acids such as acetic acid, formic acid, etc. The gel forming ability of chitosan in its application in drug release formulations has been reported (Kumar, 2000). Chitosan gives viscous solution when dissolved in acidic solutions. Hydrogel formation and viscoelastic behavior determines its potential use as thickener and other applications (Chattopadhyay & Inamdar, 2010). There are also studies implicating that chitosan flakes proven to have a high oil removal percentage of 87.5 in treating palm oil waste (Sofian, 2008). Based on all these findings, application of chitosan as a better alternative adsorbent for the treatment of emulsified wastewater will be an expanded interest in the near future.

2.4 Treatment Method: Adsorption

2.4.1 Adsorption Theory and Rationality of Adsorption Method

Adsorption method is considered as one of the few direct and economical method of breaking emulsions in wastewater (“Pollution Prevention Guidance Manual for the PFPR Industry”, 1998). Among others are filtration, foam flotation, ion exchange, aerobic and anaerobic treatment, electrolysis, coagulation, solvent extraction and adsorption. Adsorption is considered as an ideal treatment due to the process’s fundamental design and direct procedures unlike aerobic treatment which is time consuming (Bhatnagar & Sillanpaa, 2010). Adsorption method is being extensively used in organic and inorganic micropollutants removal from aqueous solutions (Lin, 2008).

Physical adsorption method will be employed in this study. This physical treatment method would be an ideal procedure due to the fact that it is considered the best way of treating wastewater as it is economical, has simple standard operation procedures and has a removal capacity of up to 99.9% (Ali et al., 2012). Adsorbate is the pollutant from the waste that is being adsorbed and the adsorbent is the adsorbing phase in this study. Adsorption processes one or more components of a gas or liquid stream are adsorbed on the surface of a solid adsorbent and a separation is accomplished. Chiefly, adsorbents are produced in the form of granules, flakes, powder and small pellets ranging from 0.1mm to 12mm in size (Peavy et al., 1985).

2.4.1.1 Adsorption Technology

There are basically four main processes and cycles in adsorption technology and design such as

- a) Fixed and moving bed processes
- b) Fixed bed processes
- c) Moving bed processes
- d) Batch processes

a) Fixed and moving bed processes

These two beds are used together in a system to get the best of both processes. Fixed vessels and columns which houses the adsorbents are at the initial stage followed by moving bed at the later stage.

b) Fixed bed processes

This process is used because the equipment is economical to fabricate and is direct. It also reduces the adsorbent losses as it is in fixed bed position although there might be fluctuation in pressure and flow directions which may be unwholesome. The cons are that it is still a practical industrial problem now. On top of that, there will be an imbalance in adsorption movement. A new, fresh fixed bed of adsorbent will receive a feed of adsorbate molecules. As fluid passes the column, the transfer of adsorbate starts at the entrance until it become saturated then it progresses towards the exit. As discussed by Crittenden and Thomas (1998), it is necessary to take the bed off-line for regeneration of adsorbent after the whole mass transfer zone (MTZ) do not participate in the mass transfer process anymore. It pauses the transfer process. Adsorbent will be in the same equilibrium as the adsorbate when the MTZ is not occurring. Meaning that no adsorbate will be adsorbed.

In addition, it is very costly to fit in a large amount of adsorbent if the bed is long. Pressure drop will be another parameter to worry about. Contrary, there is a 3-bed system which is able to minimize the extensive use of expensive adsorbent and to maintain the size of reactor. Switching between 3 different beds to improve efficiency of MTZ and the cycle to be repeated. The regeneration time for the second bed must be shorter than the time to reach breakthrough of the adsorbate during adsorption in the first bed. This is to ensure a continuous smooth operation (Crittenden & Thomas, 1998). The usage of more complex pipelines and valve arrangements will be employed together with a control system if there is more than one bed involved. Desorption can occur if the temperature of the adsorbent rises since adsorption is an exothermic process (Crittenden & Thomas,

1998). On top of that, poor heat transfer will cause longer heating and cooling time which then creates the need for bigger sized bed.

c) Moving Bed Processes

Moving bed improves the efficiency of the regeneration of adsorbent. Heat transfers are easier to handle than the fixed bed. On the other hand, a more complex and expensive equipment are required in fabrication of moving bed.

d) Batch Processes

This is considered as the simplest and direct way in mixing a batch of adsorbent with a batch of fluid. The adsorbent moves along the walls of the container. After a desired stirring, the adsorbent can be removed via sedimentation, filtration for further usage from recycling, reuse or disposal. Adsorbent such as activated carbon are used in slurry form to improve reaction and allow easier mixing. The spent activated carbon can be retrieved as settled sludge. One technique of a more economical way of preventing the use of excessive adsorbent is by using multiple batches or cross-flow system. The raw feed will be used together with a fresh adsorbent in the first batch. Spent adsorbent is to be replaced with a fresh adsorbent for the second batch (Crittenden & Thomas, 1998).

Batch process will be employed in this research due to its simple method which is ideal for this exploratory works to show the adsorption and coagulation performance of adsorbent RSSAC and chitosan respectively.

2.4.2 Potential Adsorbents

This research is focused on the use of natural adsorbents, RSSAC instead of synthesized adsorbents. Anyhow, widely used commercial adsorbent will also be briefed in this section of the literature review. Among commercialized adsorbents are activated carbon, silica gel, activated alumina, zeolites, molecular sieves and other synthetic polymers.

2.4.3 Commercial Adsorbents

a) Activated Carbon

Activated carbon proven to be able to adsorb specific organic compound that causes undesirable taste, odor and color. It is used also because it has been proven to be able to further remove Chemical Oxygen Demand (COD) level. COD or also known as refractory organics will still be in the effluent even after primary and secondary treatment. This is because of the presence of some soluble organic matters that are unable to breakdown (Davis, 2010). COD values are usually 30 to 60mg/L after secondary treatment.

Activated carbon is the best material to adsorb these refractory matters (U.S. EPA, 1979). It can be regarded as the most popular employed adsorbent in wastewater treatment in the world. A versatile adsorbent and wide usage, it is proved in the publication by Bhatnagar and Silannpaa (2010), activated carbon able to remove various types of pollutants from dyes, metal ions, phenols, detergents, humic substances and other chemicals and organisms. Activated carbon is generally nonpolar or only slightly polar because of the oxide groups and inorganic impurities on the surface (Yang, 2003). These properties made them so special in a way that they are the only commercial adsorbent used for purification and separation without the need of prior moisture removal, such as is required in air purification process. Same goes to liquid treatment processes.

Secondly, able to adsorbs more nonpolar than other sorbents because of its spacious, easy access internal surface and large pore volume. Less energy needed for regeneration and also the bond strength is lower on it than other adsorbents because only van der Waal's forces are the only acting forces.

Granular activated carbon (GAC) is used to remove excess undesirable color and odor. GAC is chosen instead of powdered activated carbon (PAC) because GAC is a more economical alternative, allows higher adsorptive capacities and easier process control (Edzwald, 2011). GAC are reported to be used in fixed bed or moving bed column with fixed bed being the most common. Down flow columns are recommended as it can function as both adsorption and filtration process. These GAC can be backwashed to remove excessive fouling build up after a certain period. Fraction PAC tends to be discharged out together with the effluent due to its fine size.

Activated carbon has been a commercialized adsorbent for its efficiency in adsorption process but there are limitations too. It is costly, regeneration of it produces a little additional effluent which is unwholesome (Geankoplis, 2003). It is also hardly being practiced in large scale usage.

b) Silica Gel

It is mesoporous which means that its pores are generally larger than 20 Å which made it a good desiccant. Silica gel is largely used in drying process due to its large water capacity and lower temperature in regeneration process also. Able to capture water up to approximate 40% by weight and temperature of 150°C compared to 350°C need for regenerating zeolites. It can absorb large amount of water at low humidity and carries the highest water capacity. Silica gel can be modified into producing many other uses. Its surface can be readily modified for applications in chromatography. Silica gel will not be used in this research since its specifications are focused on drying process.

c) Activated Alumina

Activated alumina is also widely used in drying process. It has the same advantages for which silica gel is used. The difference is that activated alumina is a crystalline and not an amorphous. This causes oxygen vacancies to form on its surface. The surface can be easily modified by treatment with acid or alkaline and controlled thermal treatment. It is a more robust and has higher selectivity in its application as a sorbent. Among the proven application of activated alumina are removal of acid from

gases and liquids, removal of acidic gases (CO_2 , H_2S , CS_2) from hydrocarbons, removal of oxygenates and Lewis Bases, removal of polar organic compounds, alkalized alumina for SO_2 removal and removal of Cl^- and F^- from water (Yang, 2003). With its widely usage as a desiccant, it has also been used in water treatment. Many studies have been done on the removal of arsenic and fluoride from water. It is effective for adsorption of As^{5+} but it is dependent on the pH value and need for acid-base titration for manipulate the charges so that to choose either anion or cation to be adsorbed based on the zero point charge. On the other hand, alkalized alumina is a commercial adsorbent for flue gas desulfurization. Activated alumina too will not be used due to the fact its specifications are focused on drying process.

d) Zeolites and Molecular Sieves

It has primary structural units which is the tetrahedra of SiO_4 and AlO_4 . Zeolites are crystalline aluminosilicates of alkali or alkali earth elements like sodium, potassium and calcium. These zeolites can be arranged in various ways resulting into larger crystalline structure. Al or Si in the zeolite can be replaced with other can produce molecular sieves. The surface of zeolites comprises mainly of oxygen atoms with Si and Al are inside of the framework. They are not exposed and cannot be accessed by adsorbate molecules. There are some that are located above and are fully accessible. Its adsorption efficiency depends on the interaction between the charges of the molecule itself and the surrounding adsorbate molecules (Yang, 2003).

These commercialized adsorbents carries high procurement costs especially when the reactor is long and are not feasible in generating a low cost yet biodegradable treatment system.

2.4.4 Low-cost Agricultural Waste as Substitute Adsorbents

Malaysia's tropical rainforest and weather is ideal for various crops and plantations. Based on the Industrial Crop Statistics 2011 by the Department of Agriculture Malaysia, it is shown that the planted area is at a staggering 174, 461.1 Ha which could produce up to 981, 351.6 Mt of agricultural crops. These crops will be harvested from time to time whole year round all over the country. Products will be exported and also for domestic use. Rubber, oil palm, cocoa, black pepper and tobacco are the five main crops with the highest industrial yield in Malaysia.

Production of these commodities will definitely generate wastes during harvesting and processing. Due to its abundance, high fractions of bio-sorbent can be produced at a lower cost (Oladoja, 2007). There is a huge fraction of agricultural wastes that contains cellulose which was proven to be able to have chelation behavior for various pollutants (Bhatnapar & Sillanpaa, 2010). These wastes are completely environmental friendly and have high economical aspect. Moreover, it is a renewable resource and available in abundance especially in Malaysia. Elsewhere, there is an expanding interest in producing natural low-cost alternatives to synthetic polymers or resins (Crini, 2006).

Processing of these wastes into low-cost adsorbents is definitely an assuring choice to be explored since it is able to reduce cost and solve environment issues. Adsorbents from peels, seeds and shells of various agricultural wastes have been practiced in the industry. Among those are chestnut shell, hazelnut shell, coconut shell, almond shell, orange peel, etc. have been used to remove toxic contaminants in water (Bhatnapar & Sillanpaa, 2010). Besides that, among other industrial wastes are saw dust, rice husk, and other tannin-rich materials which can be made into adsorbents (Ali et al., 2012).

In addition, papaya seeds have proven to be able to adsorb methylene blue by batch process. The data fits the Langmuir model and have a maximum capacity of 555.55mg/L. Besides that, tamarind seeds and palm seed coat were also used as adsorbent of chromium and o-cresol respectively. Majority of the processes are found to be at equilibrium at a low pH value of 1.12 to 1.46. Guava and mango seeds were

also reported in the use to remove phenols and dyes from waste. The stem from pineapple waste has successfully proven to be able to adsorb methylene blue as well (Bhatnagar & Sillanpaa, 2010).

2.4.5 Rubber seed shell as Adsorbent

The RSS from the rubber tree (*Hevea brasiliensis*) will be used as a bio-sorbent in this research. The Hevea tree produces latex. It is a widely developed material in almost every industry. There are studies on the extraction of rubber seed oil from the kernel as well. The RSS instead is used as biofuel or is thrown away and allowed to decompose (Oladoja, 2007).

Interestingly, RSS was used in previous studies on the removal of phenol. It was done using a batch and column processes which follows the first order kinetics and fit both Langmuir and Freundlich isotherm models (Rengaraj et al., 2001). In addition, RSS was also employed to produce activated carbon as well and was used in basic blue 3 (BB3) removals from aqueous solutions (Bhatnagar & Sillanpaa, 2010). This somehow shows the promising feature of RSS as an adsorbent alternative. The performance of RSS in emulsified wastewater was not found in any of the published literature.

Different agricultural waste was used as adsorbents for the removal of certain pollutants from water. All provide their specific adsorption capacities and isotherm models respectively. Rubber seed coat is used to remove BB3 with adsorption capacity of 227.27mg/L.

Rubber seed and its kernels comprised of tannins and other products. The tannins were found in the shell portion of the rubber seeds (Narahari & Kothandaraman, 1983). Tannin structure consists of multiple aromatic rings that can be introduced into polymerization process which further leads to coagulant or adsorbent production (Sharma & Sanghi, 2012). Tannin is a common name for large polyphenol compounds taken from natural substances. A study on tannin for water treatment works proves to be an excellent alternative material to chemical material. It is due to the phenolic groups attached in the polymer indicates that it is anionic in

nature. It further leads to the fact that the more phenolic groups available, the more effective its treatment capability.

Investigation on the characteristics of rubber seed coat carbon (RSCC) as a promising adsorbent had been done by Rengaraj et al., 2001, and is compared to the commercial activated carbon (CAC).

Table 2 - 2 : Characteristics of rubber seed coat carbon and commercial activated carbon. Adapted from “Removal of phenol from aqueous solution and resin manufacturing industry wastewater using an agricultural waste: rubber seed coat” by Rengaraj, et al., 2001, Journal of Hazardous Materials, B89, p. 185.

S. no.	Control tests	RSCC	CAC
1	Bulk density (ml)	0.70	0.68
2	Moisture content (%)	14.52	12.57
3	Ash content (%)	0.93	2.91
4	Fixed carbon content (%)	99.07	97.09
5	Matter soluble in water (%)	1.16	1.55
6	Mater soluble in acid (%)	1.92	4.58
7	pH	8.10	9.2
8	Decolourising power (mg/g)	83.2	73.5
9	Phenol number (mg)	9.02	5.15
10	Ion exchange capacity (mg/g)	Nil	Nil
11	Surface area (m ² /g)	598	296
12	Iron content (%)	Nil	Nil

For the same percentage of 96% of phenol removal, a lower dosage of RSCC is required compared to CAC (Rengaraj et al., 2001). This shows that the high carbon content in RSCC could be a potential alternative to be exploited in other than phenolic wastewater such as emulsion waste and so on.

Referring to carbon content of RSCC, there are many literatures discussed about the effects of carbonizations of RSS. Among significant ones is the temperature. Temperature affects the density, pH, adsorption strength and conductivity. This is due to porosities formed in the RSS structure when it is heated to a certain temperature.

This theory applies to other kinds of wood fibers and tannin products as well. Leading to that, these porosities give the RSS a certain specific surface area, chemical and physical reaction properties such as adsorption capacity and diffusion rate. At

temperature 600°C, RSS gives the highest adsorption number of 66.75 iodine mg/100g (Ekebafé et al., 2012). This proves that the maximum surface area was obtained at this temperature.

Lower temperature will give a lower porosity number due to incomplete carbonization. On the other hand, if the temperature exceeds 600°C, its porosity will be lower as well due to the fact that a fraction of cavities might have been burned and therefore reducing number of active surface area (Ekebafé et al., 2012).

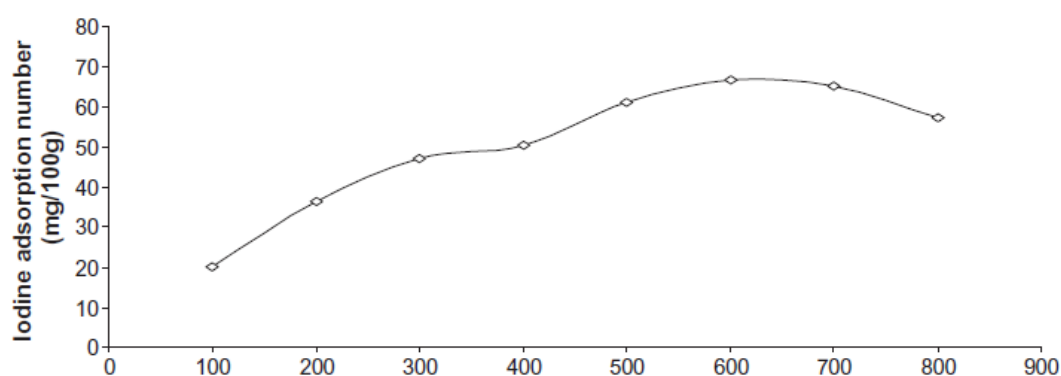


Figure 2 - 2 : Variation of iodine adsorption of RSSC with carbonization temperature. Adapted from “Effect of carbonization on the processing characteristics of rubber seed shell” by Ekebafé, et al., 2012, Arabian Journal of Chemistry, 1878-5352.

On a separate study, it is also proven that temperature gives the most significant effect in RSSAC production. At a low temperature, the rubber seed consists mainly of micropore structure. However, when the carbonization temperature increases, the pore structure enlarges and also increases the total porosity value. At high temperature, the micropores expand due to the collapsing walls of the micropores (Sun & Jiang, 2010). This concludes that RSSAC characteristics are an important element in considering it as an adsorbent. At maximum porosity will give the maximum adsorption capacity.

RSSAC has been proven to have high commercial aspect and as a high efficiency adsorbent. In addition, low cost adsorbent employed from shells of different agricultural waste have been examined by various researchers for the

treatment of wastewater. This can be lead to the future of RSSAC as a potential natural adsorbent.

2.5 Treatment of Industrial Wastewaters

There is a slight issue on the matter that many natural coagulants and adsorbents are unable to cater for industrial use. This might due to the fact that their low availability since rubber seeds and other agricultural products breed, flowers and harvested according to certain season of the year. But its advantages somehow could offset its disadvantages. The usages of these natural materials are sustainable, non-toxic, environment friendly and able to form stronger flocs via bridging effect compared to alum (Yin, 2010). This lead to the fact that it is best to be used within a batch stirred tank reactor to treat contaminated industrial wastewater because it has strong flocculation properties which can be easily controlled by mechanical forces.

2.6 Conclusion

As a conclusion, researches on the coagulation and adsorption performance of chitosan and also RSSAC on the development of emulsified wastewater treatment system are insufficiently conducted and are hardly reported in the literature. On top of that, there are no publications of water treatment performance in comparison of chitosan and RSSAC. Natural polymer chitosan and a more economical bio-sorbent, RSSAC will be assigned and developed to study its feasibility in reducing the pH, TSS, O&G and turbidity of waste aligning with the other parameter limits of effluent of Standards A and B regulated by the Environment Quality Act, 1974.

3.0 MATERIALS AND METHODS

3.1 Experimental Materials

Approximately 50kg of emulsified wastewater were collected from Vacuumschmelze (M) Sdn. Bhd, Pekan, Pahang. The collected samples was placed in a plastic container, sealed tight and labeled, before it was transported back to the laboratory. Samples were then refrigerated at about 4 °C to prevent bio activities from occurring. Analysis was done within 6 to 24 hours of collection from the plant (APHA, 2005).

Chitosan was purchased from Hunza Nutraceuticals Sdn. Bhd. in powder form with viscosities and DDA are about 30-3000mPa.S (at 25°C) and 85-98%. 50kg of local fresh rubber seeds were purchased from NDI Utara Enterprise. Proximate analysis of local rubber seeds consists of 3.99% moisture content, 17.41g/100g protein, 68.53g/100g fat and ash content of 3.08g/100g (Nadiyah et al., 2010).

Analytical grade chemicals are purchased from various sources namely, Fisher Scientific, Sigma-Aldrich, Merck Group, Permula Chemicals and Euroscience.

3.2 Parameters

Four major parameters from the Standard A and B Water Quality Limits will be reviewed in this research.

Table 3 - 1: Significance of parameters monitored in this research.

Parameter	Rational
pH	pH causes synergistic effects that determine the toxic effects of certain substances such as zinc, iron etc. (“Kentucky Water Watch”, n.d.). To study the effect of pH after treatment.
TSS	Such materials are organic and biological in nature and may cause diseases and toxic algae (Peavy et al., 1985).
O&G	Oily wastewater such as machine coolants from metal manufacturing machining contains high concentration of O&G and are difficult to treat (Wang et al., 2006).
Turbidity	Emulsifying agents results in turbidity which may cause undesired taste, odor and aesthetically displeasing “milky” coloration. Turbidity may prevent light penetration and photosynthetic reactions in water streams (Peavy et al., 1985).

These four parameters are important especially in emulsified wastewater because of the nature of the wastewater that contains high amount of TSS, O&G and turbidity which is due to the emulsifying agent, oil residual and rusted metal.

3.3 Preparation of chitosan and RSSAC

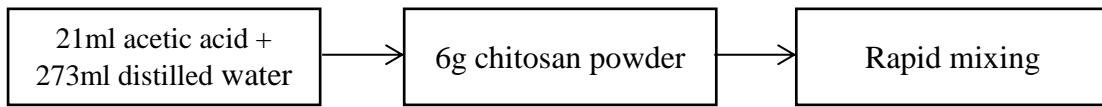


Figure 3 - 1: Activation of chitosan

Chitosan powder was used as a starting material in this work. The procedures for activation of chitosan was prepared by diluting it with acetic acid as discussed by Rinaudo et al., (1999) to produce a gel-like substance. Dilution was conducted by using a self-estimated 2:7:91 ratio of chitosan to acetic acid to distilled water to produce a certain chitosan concentration. 21ml of acetic acid was added into 273ml of distilled water. 6g of chitosan powder was later added slowly into the stirring solution to improve well mixing and was stirred rapidly for 15 minutes. The prepared 300ml of chitosan coagulant was stored in a beaker for further use.

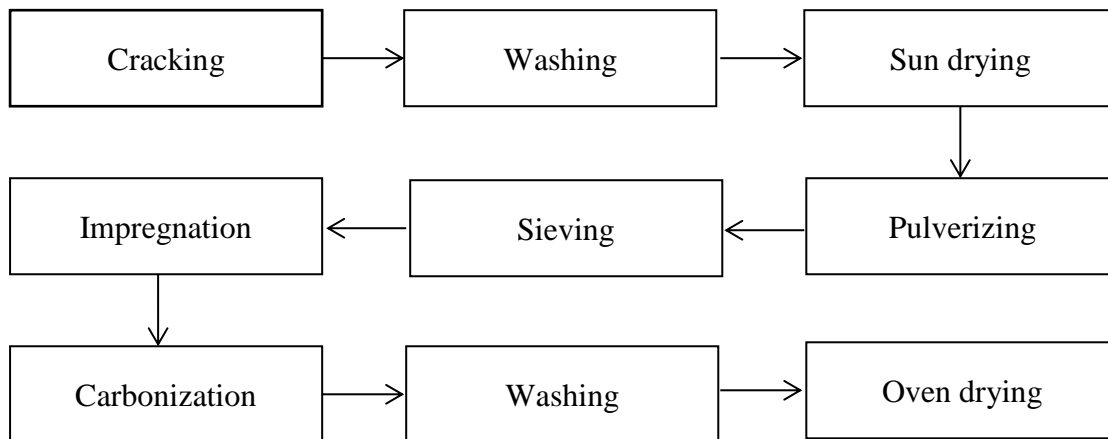


Figure 3 - 2: Preparation of RSSAC

Based on Figure 3-2 above, 30kg of fresh rubber seed was cracked to get the shell which was then washed repeatedly with deionised water to remove dust and dirt, sun-dried, pulverised and sieved into particle size of 162 μm . The powdered rubber seed shell was activated chemically by impregnation with NaOH at a ratio of 1:1 of dry weight of RSS powder to NaOH. This was done by dissolving 30g of NaOH into

300ml of distilled water before adding 30g of RSS powder into the solution and was stirred with a spatula. The degree of impregnation is defined by

$$\text{Impregnation ratio} = \frac{\text{Weight of active agent}}{\text{Weight of carbonizing material}} \quad \text{eq. (1)}$$

The mixture was left to stand overnight to make sure the chemicals are fully adsorbed into the RSS. The impregnated RSS was then transferred into crucibles and covered with lid before being carbonized in a furnace to produce RSSAC. The carbonization temperature was manipulated at 450°C, 650°C and 850°C under nitrogen gas flow rate at 120ml/min for 120 minutes. The produced RSSAC was left overnight to be cooled to room temperature and then washed by filtering hot distilled water through it to remove any NaOH residue. The moist RSSAC was then dried in the oven at 80°C overnight and stored for further use.

3.4 Experimental Procedures

The Jar Test apparatus was used treat emulsified wastewater. A repetition of jar test experiment is the standard technique for adjusting chemical dose (Davis, 2010). Bigger scale and faster methods as an alternative to jar test such as zeta potential measurements and the application of streaming current detector (SCD) are available but it is unnecessary and will not give a much difference in this exploratory research.

It was conducted in a batch test with a row of six beakers each having a stirring device. One jar was used as a control and the other five were of different dosages of chitosan. Experiment was repeated by varying the mixing speed. RSSAC was used as a secondary treatment at a later stage.

After the desired dosage of coagulant was added, the beakers were stirred violently to promote rapid mixing at 250rpm, simultaneously. Rapid or flash mixing is practiced to disperse the coagulants and to initiate the particle aggregation process to ensure uniform distribution of coagulants in the treatment (Amirtharajah & Mills, 1982). The agitation speed will be then lowered constantly to promote the formation of flocs (Peavy et al., 1985). A sample will be taken using a pipette from the bottom

inch of the beaker for analysis. Analysis for desired parameter was done for treated water with chitosan and also the combined chitosan + RSSAC.

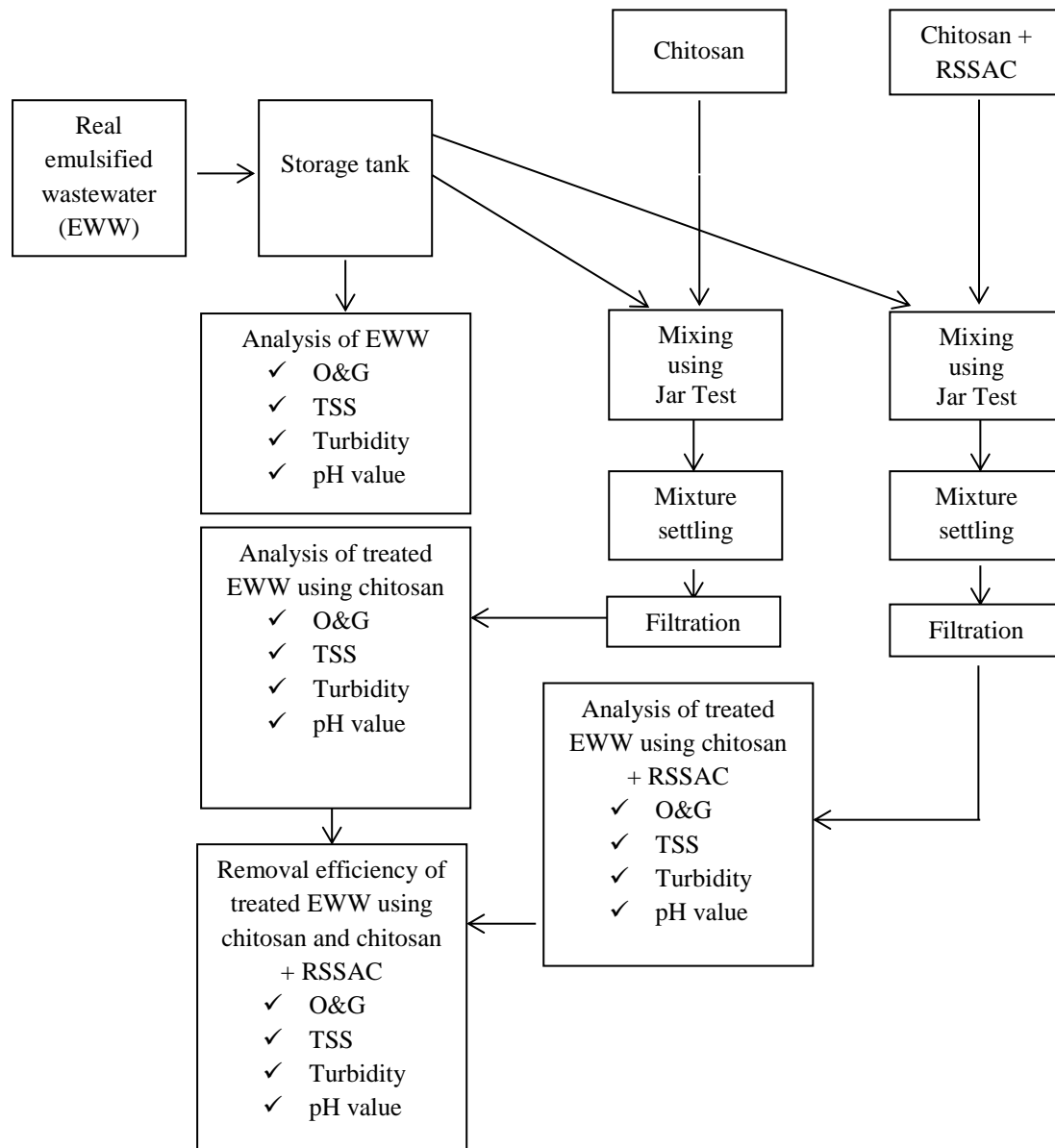


Figure 3 - 3: Schematic diagram of treatment of emulsified wastewater

3.5 Laboratory Analysis

The analysis of the treated sample was carried out in the Environmental Engineering Lab of the Faculty's Laboratory. Parameters pH, TSS, O&G and turbidity was analyzed. These methods are based on the Examination Manual of Water and Wastewater, APHA (2005). Hexane Extractable Gravimetric Method was used for O&G due to its feasibility in this study because it can handle emulsions that are stubborn formed by organic matters and there are available equipment and reagents needed in the faculty's laboratory.

Table 3 - 2: Summarized experimental analysis method.

Parameter	Analysis Method	Analytical Equipment
pH	pH meter and probe	SevenEasy pH-METTLER TOLEDO
TSS	Gravimetric Test involving the mass of residues	Laboratory apparatus
O&G	Hexane Extractable Gravimetric Method	Laboratory apparatus
Turbidity	Electronic Turbidity Meter	HACH 2100P

Table 3-2 summarizes all the methods which was employed and conducted for the analysis of treated sample.

4.0 RESULTS AND DISCUSSIONS

4.1 Results of produced RSSAC

The preparation conditions, BET surface area (S_{BET}), total pore volume (V_T) and average pore diameter (D) of the produced samples are listed in Table 4-1. The S_{BET} and V_T of the RSSAC are higher than the values of activated RSS besides the D . Carbonization is able to increase the S_{BET} up to 20 folds. Results from Table 4-1 shows the highest reading of S_{BET} ($19.2403\text{m}^2/\text{g}$) and V_T ($0.097638\text{cm}^3/\text{g}$) were seen at 650°C for carbonization time of 120 min compared to S_{BET} ($0.9482\text{m}^2/\text{g}$) and V_T ($0.007379\text{cm}^3/\text{g}$) before carbonization. The S_{BET} increases with increase in temperature until 850°C where it starts to decline slightly to S_{BET} ($14.8239\text{m}^2/\text{g}$) as shown in Figure 4-1. The V_T follows the same trend as well and decreased slightly to V_T ($0.072154\text{cm}^3/\text{g}$). On the other hand, the D decreases from 29.9485nm to 16.4818nm at the temperature of 650°C and experience sudden increase to 24.0422nm at 850°C .

Table 4 - 1: Results of produced activated RSS and RSSAC.

Treatment	Temperature ($^\circ\text{C}$)	BET surface area, S_{BET} (m^2/g)	Total pore volume, V_T (cm^3/g)	Average pore diameter, D (nm)
Activation (RSS)	80	0.9482	0.007379	29.9485
	450	2.1290	0.006841	27.2524
Carbonization (RSSAC)	650	19.2403	0.097638	16.4818
	850	14.8239	0.072154	24.0422

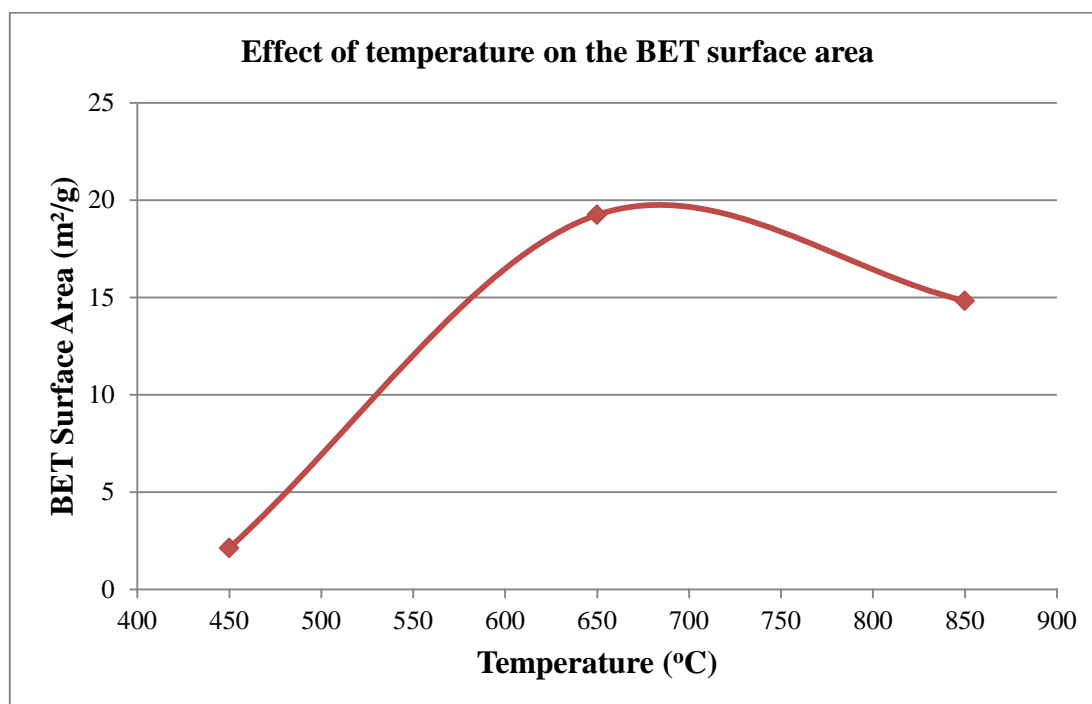


Figure 4 - 1: Effect of temperature on the BET surface area of RSSAC. Carbonization time = 120 min.

Carbonization is able to remove volatile compounds and promotes formation of new pores (Borhan, 2012). It can be seen that the carbonization temperature will have a significant effect on the pore structure of the sample. With the increase in carbonization temperature, the mesopore structure is created from the existing micropore structure at low temperature. Thus, lead to the increase in V_T as well (Ismadji, 2001). The geometrical structural change is due to the enlargement of the micropores when the pore wall collapsed, forming the mesopores (Sun, 2008).

On the other hand, the values dropped when the carbonization temperature is increased to 850°C. This is because extreme temperature will lead to the rupture of some porous wall, which causes lower porosity formation (Borhan, 2012). It also indicates over activation which increases surface erosion rather than the desired pore formation (Kiyoshi et al., 2003). A literature suggested that the ideal conditions were obtained at temperature of 500°C and activation time of 180 min and the S_{BET} value starts to decline at 600°C (Borhan, 2012). High value of S_{BET} can be obtained at temperature of 800-900°C but it is for physical activation with gas which is not in the scope of this study.

The bio-adsorbent prepared from RSS was studied for its efficiency in emulsion wastewater treatment in combination with bio-coagulant chitosan under different experimental conditions. The outcome of the relevant results and observations are discussed in the following sub topic.

4.2 Characterization results of emulsified wastewater

Samples of emulsified wastewater have been obtained and characterization study was done. Parameters of the emulsified wastewater were compared with the standard water quality parameter limits set by the Ministry of Health Malaysia. Discrepancy and comparison of the focused parameters is discussed in this chapter. This provides a standard guideline to be compared with the treated wastewater.

Table 4 - 2 : Characteristics of raw emulsified wastewater in comparison with the parameter limits of effluent of standards A and B.

No	Parameter	Unit	Standard A	Standard B	Raw Emulsified Wastewater
1	pH	-	6.0-9.0	5.5-9.0	9.71
2	BOD ₅ at 20°C	mg/L	20	50	63
3	COD	mg/L	50	100	57770
4	TSS	mg/L	50	100	More Than 750
5	Mercury	mg/L	0.005	0.05	1.1146
6	Cadmium	mg/L	0.01	0.02	0.000
7	Chromium, Hexavalent	mg/L	0.05	0.05	9.4

8	Arsenic	mg/L	0.05	0.10	0.002
9	Cyanide	mg/L	0.05	0.10	-
10	Lead	mg/L	0.10	0.5	0.135
11	Chromium, Trivalent	mg/L	0.20	1.0	1.4
12	Copper	mg/L	0.20	1.0	0.252
13	Manganese	mg/L	0.20	1.0	0.000
14	Nickel	mg/L	0.20	1.0	0.000
15	Tin	mg/L	0.20	1.0	5.498
16	Zinc	mg/L	1.0	1.0	34.664
17	Boron	mg/L	1.0	4.0	0.000
18	Iron (Fe)	mg/L	1.0	5.0	0.000
19	Phenol	mg/L	0.001	1.0	More Than 2.5
20	Free Chlorine	mg/L	1.0	2.0	29
21	Sulphide	mg/L	0.50	0.50	11.8
22	Oil and Grease	mg/L	Not Detectable	10.0	More Than 100

Table 4 - 3 : Physical properties of raw emulsified wastewater.

No	Parameter	Unit	Results
1	Viscosity	cP	132.6
2	Turbidity	NTU	70
3	Density	g/cm ³	1.001

Table 4-2 and Table 4-3 above list the values for the tested parameters of emulsified wastewater sample before treatment processes. Standard A is a more stringent list compared to Standard B. This is because Standard A is applied as a regulation at the water catchment areas which includes areas upstream of surface or above sub-surface of waterways, mainly directed to the community and for human use.

On the other hand, Standard B applies to effluent that leads to the downstream waterways such as the sea (Environmental Quality: Sewage and Industrial Effluents Regulations, 1979). These limits have to be followed from time to time to ensure a safe water supply for economic use, human consumption as well as to protect the environment.

Based on Table 4-2, it is shown that the cadmium, arsenic, manganese, nickel, boron and iron concentrations from the raw wastewater complies with the standard A and B limits. These parameters are under the acceptable limits. However, parameters pH, BOD₅, COD, mercury, chromium-hexavalent, chromium-trivalent, lead, copper, tin, zinc, phenol, free chlorine, sulphide and O&G does not comply with the standards A and B. Copper concentration at 0.252mg/L complies with the standard B of 1.0mg/L but is slightly above standard A of 0.20mg/L. COD and zinc records a high value of 57 770mg/L and 34.664mg/L respectively. Chemical oxygen demand is high because of a numbers of oxidants that react within the sample. The higher the numbers of oxidants react, the higher the COD will be. As an example, dichromate ion (Cr₂O₇²⁻) is reduced to chromic ion (Cr³⁺). COD is the cause of the presence of mercury, chromium-hexavalent and acids in the raw wastewater (APHA, 2005). The presence of heavy metals such as zinc, lead, tin and hazardous chemicals phenols, free

chlorine and sulphide are due to the nature of lubricant, fouling particles from the machine itself and also the metallic product that are being produced in the process (EPA Guidance Manual, 1999).

In this research, parameter TSS, O&G, Turbidity and pH will be the main focus. This leads back to the scope of this research which is to study the performance in demulsification. These parameters are significant in order to determine the demulsification effect of the emulsion waste treatment. TSS recorded is over 750mg/L, compared to the acceptable limits of 50mg/L and 100mg/L of standard A and B respectively. Another significant parameter, the O&G is more than 100mg/L compared to the allowable 10mg/L for standard B. Turbidity of the wastewater is at 70 FAU (70 NTU) and it shows a low clarity of water and it is in milky form. 1 Formazin Attenuation Units (FAU) is equivalent to 1 Nephelometric Turbidity Unit (NTU) of formazin standard. These values are high due to the emulsion. The water droplet is covered by a layer of the emulsifying agent, therefore causing emulsions to form which lead to the high O&G value in the solution.

The O&G result from the COA shows undesirable result in a range. In response to that, the O&G analysis was repeated at the lab by using the hexane extractable gravimetric method (APHA, 2005) in order to obtain an exact value of result. The O&G residual recorded is 3657.14 mg/L.

4.3 Effect on O&G removal %

Table 4 - 4: Effect of mixing time and dosage on the O&G removal at initial oil concentration of 3657.1mg/L

Effect of mixing time			
Treatment	Time of mixing (min)	Residual oil concentration (mg/L)	O&G removal (%)
Chitosan (4.4 wt.%)	0	3657.1	0.0
	20	3027.1	17.2
	25	2514.2	31.3
	30	884.3	75.8
	35	1028.0	71.9
	40	2400.0	34.4
Chitosan (4.4 wt.%, 30min) + RSSAC (0.6 wt.%)	0	3657.1	0.0
	20	1700.0	53.5
	25	1200.0	67.2
	30	1850.0	49.4
	35	1000.0	72.7
	40	350.0	90.4
Effect of dosage			
Treatment	Dosage (wt.%)	Residual oil concentration (mg/L)	O&G removal (%)
Chitosan (30 min)	3.2	2427.1	33.6
	3.6	2741.4	25.0
	4.0	1198.6	67.2
	4.4	884.29	75.8
	4.8	1998.6	45.4
Chitosan (4.4 wt.%, 30min) + RSSAC (40 min)	Dosage (wt.%) of RSSAC		
	0.2	1750.0	52.1
	0.4	1400.0	61.7
	0.6	1550.0	57.6
	0.8	1600.0	56.2
	1.0	850.0	76.8

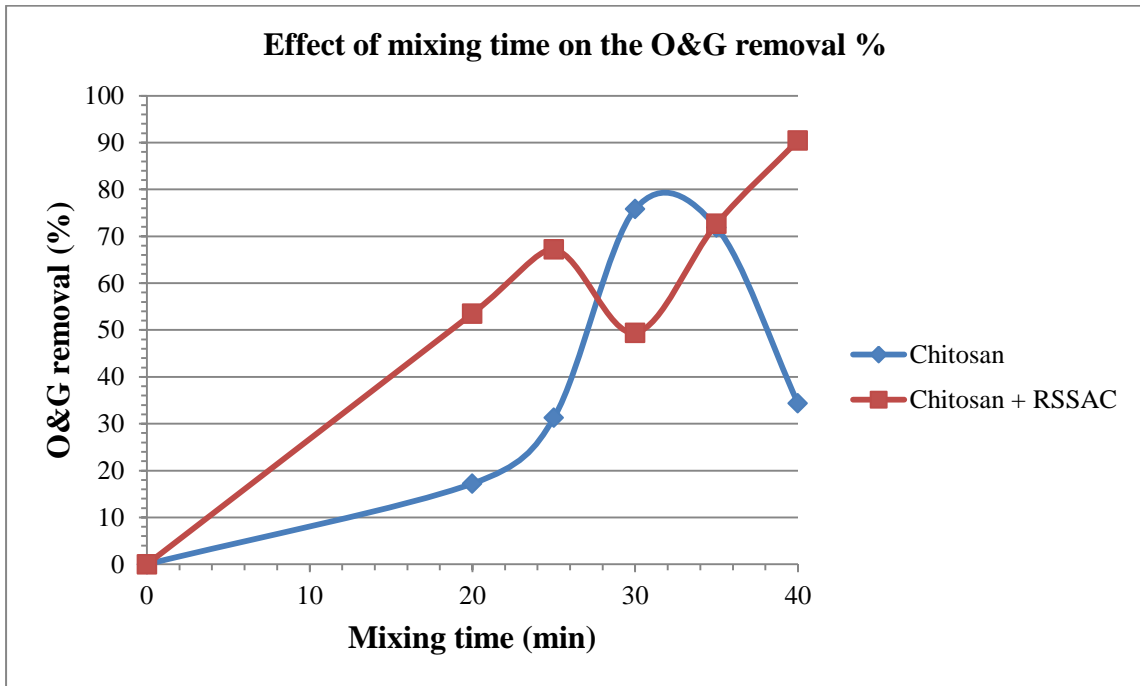


Figure 4 - 2: Effect of mixing time on the O&G removal %

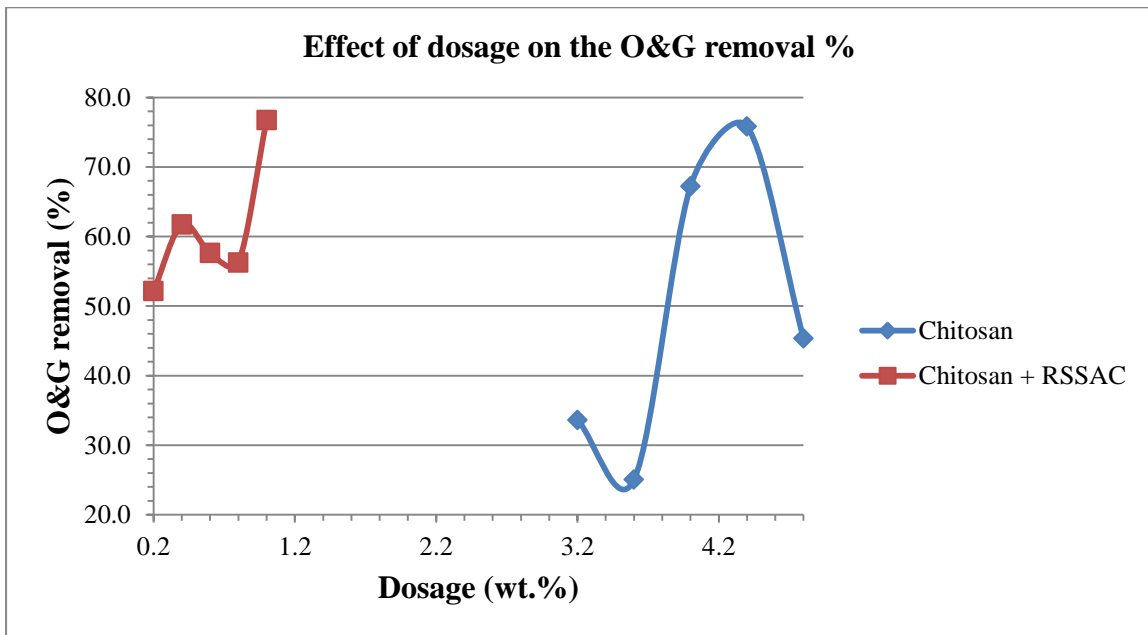


Figure 4 - 3: Effect of dosage on the O&G removal %

The effect of various mixing time (min) and dosage (wt.%) for treatment with chitosan and chitosan + RSSAC on the oil residue removal of emulsion wastewater was experimented by manipulating the mixing time and dosage with 250 rpm of mixing speed at room temperature. From Figure 4-3, the highest O&G removal by chitosan was achieved at 4.4 wt.% of chitosan with removal efficiency of 75.8%. The 4.4 wt.% of chitosan was used as a fixed variable for preparation of primary treated water for further treatment by RSSAC. At 1.0 wt.% of RSSAC, records the highest O&G removal efficiency at 76.8%. Averagely, the combined treatment shows a higher average of O&G removal % than the primary treatment by chitosan alone.

Figure 4-2 shows that at the highest mixing time of 40 min, chitosan + RSSAC bare the highest percentage of O&G removal of 90%. The combined system able to reduce 90% of O&G compared to chitosan alone only able to reduce up to 76%. It can be reasoned that the combined treatment is better than the treatment by chitosan alone in O&G removal.

This experience may be explained by the combined coagulation and adsorption action of the chitosan and RSSAC respectively. The hydroxyl groups located at the chitosan polymer are able to adsorb oil residue by forming covalent bonds. This property promotes breaking of oil droplets and at the same time demulsify the emulsion (Razali et la., 2010). On top of that, the chitosan compresses the electric double layer around the oil droplets which lead to neutralization of the repulsive forces among them. It promotes the coalescence of oil droplets. The produced low repulsion enhances the physical adsorption of the remaining oil droplets on the surface of the RSSAC which is originally negatively charged. The physical adsorption of oil molecules into the RSSAC may be explained firstly by diffusion, followed by capillary action of the oil at the RSSAC interface and lastly the aggregation of oil into the pores of the substrate (Xiaobing, 2010).

Furthermore, a paper has pointed out this effective theory by employing coagulant salt combined with saw dust as adsorbent in a continuous bed filter in treating O/W emulsions. It was reported to be able to produce oil removal ratios greater than 99% (Cambiella, 2005). Also, bentonite, powdered activated carbon and deposited carbon were employed in O/W emulsions treatment as well and able to

reduce oil residue percentage by 96.5%, 82.6% and 97.5% respectively (Okiel et al, 2010).

4.4 Effect on TSS removal %

Table 4 - 5: Effect of mixing time and dosage on the TSS removal at initial TSS concentration of 750mg/L

Effect of mixing time			
Treatment	Time of mixing (min)	TSS (mg/L)	TSS removal (%)
Chitosan (4.4 wt.%)	0	750	0.0
	20	4	99.5
	25	6	99.2
	30	28	96.3
	35	4	99.5
	40	12	98.4
Chitosan (4.4 wt.%, 30min) + RSSAC (0.6 wt.%)	0	750	0.0
	20	20	97.3
	25	24	96.8
	30	28	96.3
	35	30	96.0
	40	28	96.3
Effect of dosage			
Treatment	Dosage (wt.%)	TSS (mg/L)	TSS removal (%)
Chitosan (30 min)	3.2	4	99.5
	3.6	35	95.3
	4.0	30	96.0
	4.4	28	96.3
	4.8	8	98.9
Chitosan (4.4 wt.%, 30min) + RSSAC (40 min)	Dosage (wt.%) of RSSAC		
	0.2	66	91.2
	0.4	10	98.7
	0.6	28	96.3
	0.8	24	96.8
	1.0	30	96.0

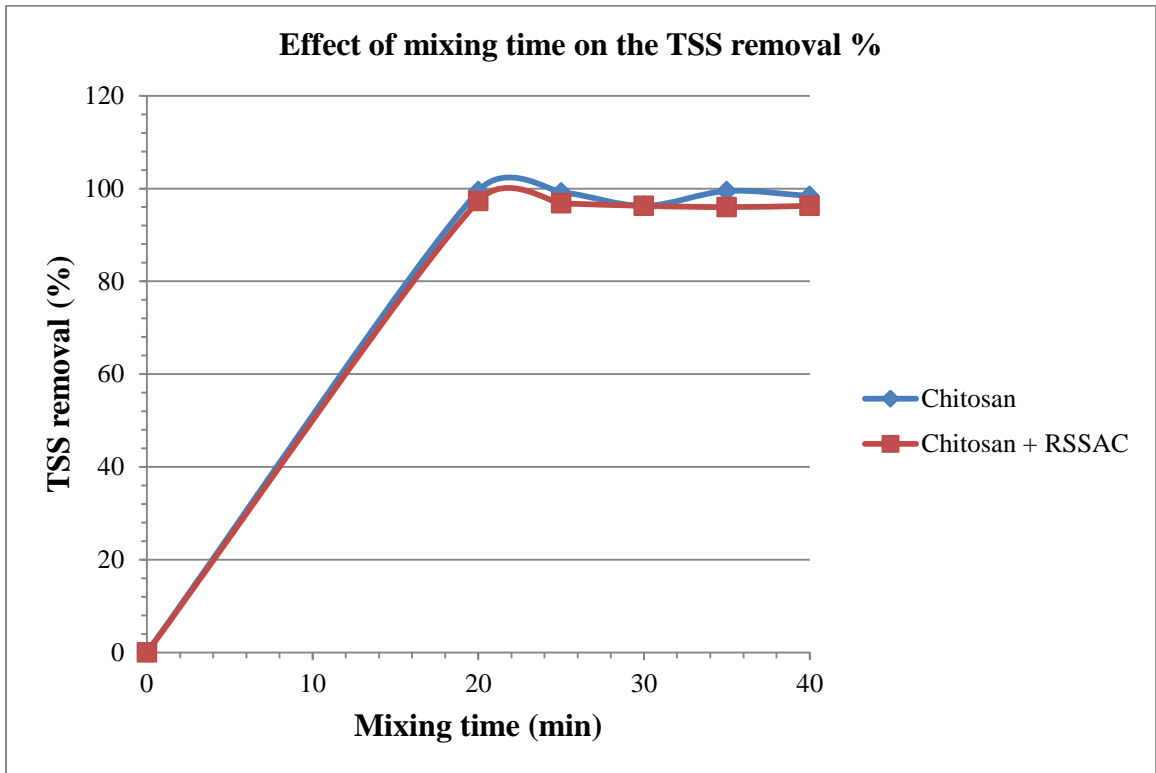


Figure 4 - 4: Effect of mixing time on the TSS removal %

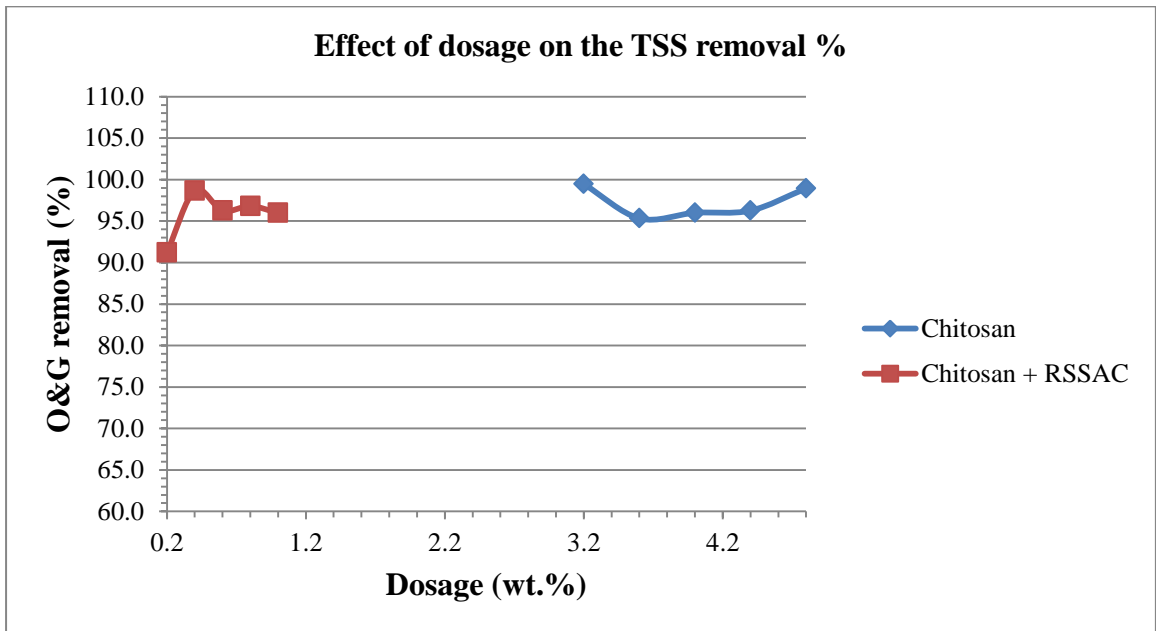


Figure 4 - 5: Effect of dosage on the TSS removal %

From Figure 4-5, the highest TSS removal of 99.5% with chitosan was achieved. However, the combined treatment together with RSSAC shows lower removal efficiency at only 98.7%. This phenomenon will be further explained in the following paragraph.

Figure 4-4 portrays a high TSS removal ranging from 96% to 99.5% for chitosan and chitosan + RSSAC combined treatment respectively. Both showed high suspended solid removal percentage from the emulsified wastewater. Chitosan is able to remove 99.5% of suspended solid while the combined chitosan + RSSAC are at 97.3%.

Chitosan is said to be able to adsorb the small particles by attachment on to the hydroxyl groups. On the other hand, the porosity in the RSSAC is able to trap and adsorb even smaller particles of various sizes of residue molecules. This is due to the existence of pore size distribution rather than a uniform similar pore sizes (Wang et al., 2012). This enables the RSSAC to be able to trap a lot of small suspended solids in the emulsified wastewater.

However, the combined system shows a slightly lower TSS removal compared to chitosan alone. This may be due to the size particle of the RSSAC. The fast qualitative filter paper during final filtration was unable to trap all the RSSAC added in for adsorption treatment. A fraction of the carbon by passes the filter paper into the treated solution, causing a slightly higher TSS reading compared to chitosan treatment.

The RSSAC was produced to have desired high BET surface area and porosity in order to achieve desired performance in trapping oil droplets by possessing a fine particle size distribution. To support the theory, the quantity of suspended solids absorbed will increase as the particle size decrease. A paper mentioned that the suspended solids in the wastewater might increase if the adsorbent size is too fine (Xiaobing, 2010). Also, the smaller the particle, the harder it is to separate. The treated water can be further purified by membrane ultrafiltration which will lead to excellent filtrate clarity (Peters et al., 2004). Also, the colour content in the treated wastewater indicates the presence of heavy metals and can be further treated to improve filtrate clarity.

4.5 Effect on Turbidity removal %

Table 4 - 6: Effect of mixing time and dosage on the turbidity removal at initial turbidity level of 70mg/L

Effect of mixing time			
Treatment	Time of mixing (min)	Turbidity (NTU)	Turbidity removal (%)
Chitosan (4.4 wt.%)	0	750	0.0
	20	2.92	95.8
	25	5.18	92.6
	30	3.55	94.9
	35	1.34	98.1
	40	2.40	96.6
Chitosan (4.4 wt.%, 30min) + RSSAC (0.6 wt.%)	0	750	0.0
	20	6.24	91.1
	25	5.37	92.3
	30	7.36	89.5
	35	5.78	91.7
	40	6.66	90.5
Effect of dosage			
Treatment	Dosage (wt.%)	Turbidity (NTU)	Turbidity removal (%)
Chitosan (30 min)	3.2	4.00	94.3
	3.6	4.00	94.3
	4.0	4.20	94.0
	4.4	3.55	94.9
	4.8	1.05	98.5
Chitosan (4.4 wt.%, 30min) + RSSAC (40 min)	Dosage (wt.%) of RSSAC		
	0.2	7.29	89.6
	0.4	6.95	90.1
	0.6	5.41	92.3
	0.8	9.10	87.0
	1.0	5.26	92.5

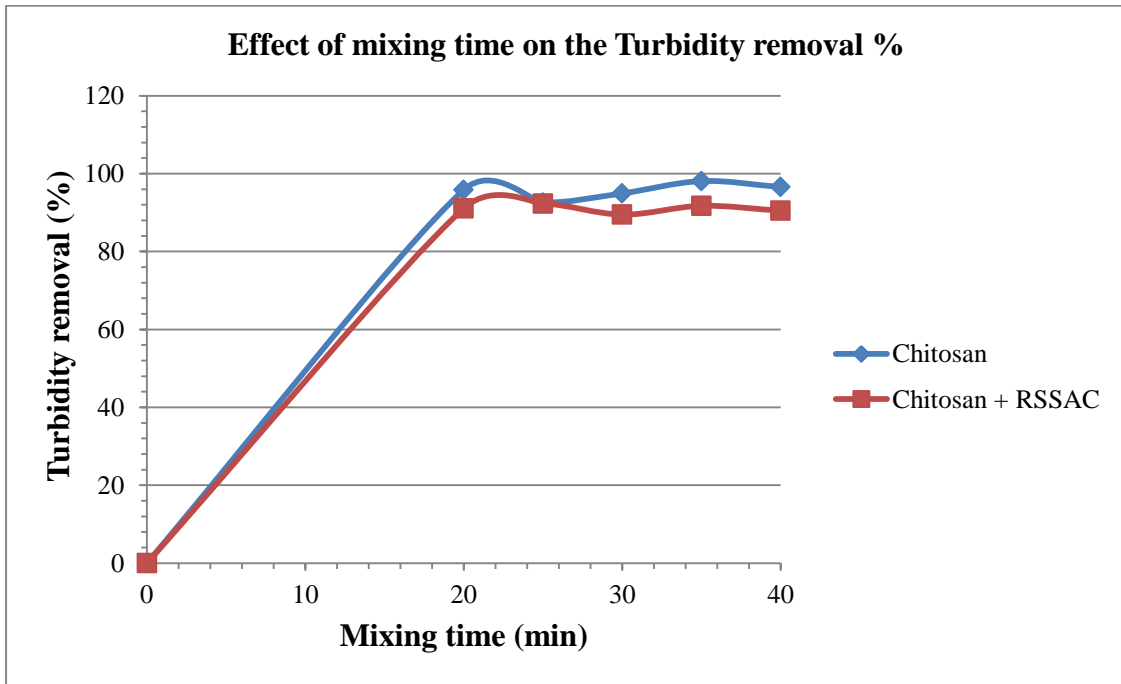


Figure 4 - 6: Effect of mixing time on the turbidity removal %

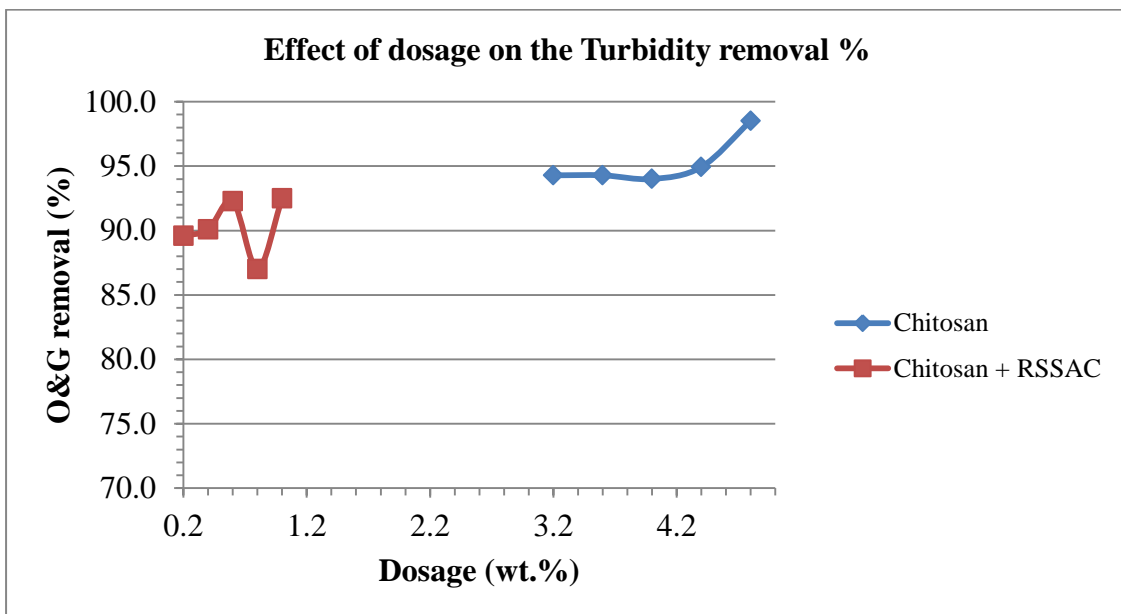


Figure 4 - 7: Effect of dosage on the turbidity removal %

From Figure 4-7, the highest turbidity removal of 98.5% with chitosan was achieved. However, the combined treatment together with RSSAC shows lower removal efficiency at only 92.5%. This phenomenon will be further explained in the following paragraph.

Figure 4-6 demonstrates the efficiency of chitosan and chitosan + RSSAC in the percentage turbidity removal. The industrial emulsion wastewater records a high initial turbidity of 70 NTU. The turbidity is reduced up to 98.1% which is 1.34 NTU at 35 min of mixing time. The chitosan treated wastewater shows a range of turbidity removal from 92.6% to 98.1% whereas the combined treatment shows a slightly lower range of 89.5% up to 92.3%.

The chitosan and RSSAC able to reduce the turbidity by agglomerating and adsorbing the particles and other impurities suspended in the emulsion waste. Theoretically, emulsion turbidity is heavily dependent on the particle size and concentration of the solution (Reddy & Fogler, 1980). Concentration of particles differs with time because of coagulation and clumping of particles by the chitosan. As mixing time progresses, it promotes coagulation and adsorption of fine particles at the pores of the RSSAC. Having high porosity and surface area, RSSAC is believed to be an appropriate material for the removal of oil and residues from the emulsion wastewater. Milky and high turbidity emulsion waste can be treated by chitosan as well as RSSAC to produce a desired low turbidity solution.

With reference to the issue encountered at the lower TSS removal due to the size of the RSSAC, the fine particles of RSSAC suspended in the treated waste also caused the turbidity to be lowered due to the presence of fine RSSAC in the solution. However, it is still able to reduce the turbidity of the raw emulsion waste up to 92.3%.

4.6 Effect on pH value

Table 4 - 7: Effect of mixing time and dosage on the pH value

Effect of mixing time		
Treatment	Time of mixing (min)	pH
Chitosan (4.4 wt.%)	0	9.71
	20	8.88
	25	9.10
	30	9.02
	35	9.07
	40	9.08
Chitosan (4.4 wt.%, 30min) + RSSAC (0.6 wt.%)	0	9.71
	20	9.11
	25	8.92
	30	8.82
	35	8.86
	40	8.89
Effect of dosage		
Treatment	Dosage (wt.%)	pH
Chitosan (30 min)	3.2	9.11
	3.6	9.11
	4.0	9.10
	4.4	9.02
	4.8	8.96
Chitosan (4.4 wt.%, 30min) + RSSAC (40 min)	Dosage (wt.%) of RSSAC	
	0.2	9.14
	0.4	9.20
	0.6	9.23
	0.8	9.26
	1.0	9.25

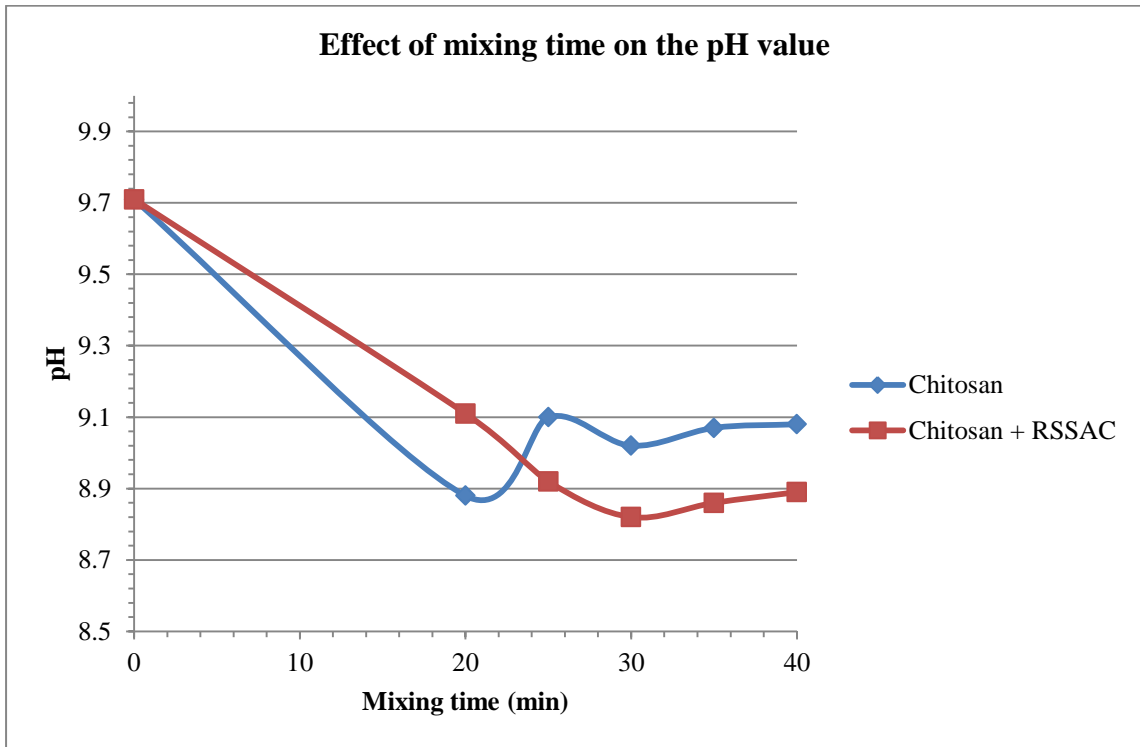


Figure 4 - 8: Effect of mixing time on the pH value

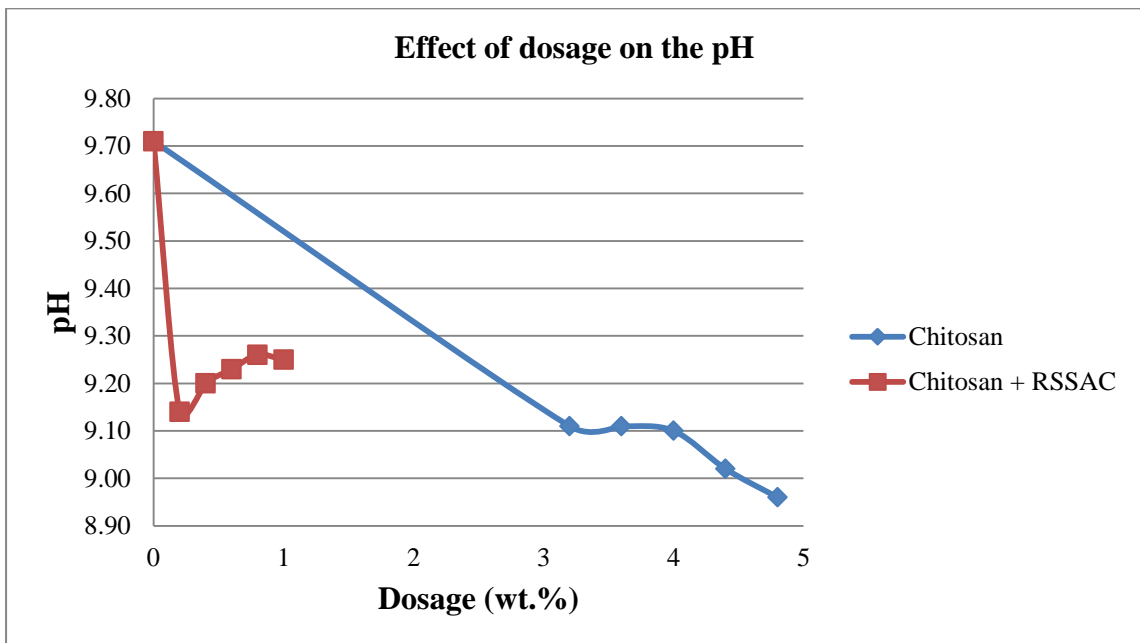


Figure 4 - 9: Effect of dosage on the pH value

Figure 4-9 shows the pH of the emulsion waste reduced from 9.71 to 8.96 and 9.14 for treatment with chitosan and chitosan + RSSAC respectively. Graph also

shows that the pH value increases consistently as the dose of RSSAC increases and the pH decreases as the dose of chitosan increases. The increase in pH by additional RSSAC dose may be due to the residual NaOH present in the RSSAC. Again, this is due to the residual RSSAC in the treated water after where the filter paper unable to trap all the fine RSSAC. But overall, it reduced the high pH of raw waste from 9.71 to 8.88.

The initial pH of the emulsion wastewater is at pH of 9.71. After chitosan treatment, the pH is reduced from 9.71 to 8.88 after 20 min of contact time. The overall average pH reduced is 9.03. For the combined treatment of chitosan and chitosan + RSSAC, the pH is reduced to 8.82 after 30 min of contact time. The overall average pH reduced is 8.92. This shows that the combined treatment have slightly more consistency in reducing the pH of the emulsion. The stability and charge density of emulsion is heavily dependent on the pH (Bratskaya et al., 2006). The interaction between chitosan and oil droplets is influenced by electrostatic mechanism and is heavily influenced by pH. At pH higher than 7.5, chitosan losses it's solubility and able to promote phase separation of O/W emulsions (Bratskaya et al., 2006).

At the present work, chitosan is able to separate the oil residue at pH 9.71. This work shows that the RSSAC adsorption capacity is not affected by the pH of emulsion since the combined system able to reduce oil residue higher than the chitosan primary treatment. However, there are theory mentioned that the adsorption capacity will be greater under acidic condition rather than alkaline (Xiaobing et al., 2010). At this work, the pH effect may be said to be negligible since it able to produce positive results on oil residue removal. Another study states that it is not necessary to adjust pH for treatment of oily wastewater after experimenting it with anthracite. The result showed adsorption capacity of anthracite only ranges from 22.0 to 25.0 mg/g over the pH manipulated. Therefore it is conclude that the raw emulsion may be treated directly without the need to adjust the pH.

5.0 CONCLUSION & RECOMMENDATION

5.1 Summary

The present exploratory works showed that low cost industrial waste, RSS can be made into a valuable activated carbon as bio-sorbent for emulsion waste treatment. The optimum settings for produced RSSAC were obtained at carbonization temperature of 650°C for 120 minutes under nitrogen gas flow after impregnation with NaOH. The BET surface area of RSSAC increases when the carbonization temperature increases until it reaches a temperature limit where it starts to decline.

The combined treatment of chitosan + RSSAC showed satisfying results in reducing O&G, TSS, turbidity and pH of emulsion wastewater. Combined coagulation and adsorption treatment in the O&G reduction of the emulsion waste showed the better results compared to treatment with chitosan alone. TSS, turbidity and pH value reduced comply with the standard A and B.

Table 4 - 8: Summary of produced optimum results

Treatment	O&G (mg/L)	TSS (mg/L)	Turbidity (NTU)	pH value
Before treatment	3657.14	750	70	9.71
Chitosan	884.3	4	1.34	8.88
Chitosan + RSSAC	350.0	20	5.26	8.82

This shows the alternative methods in treating emulsion waste by using biomaterials chitosan and RSSAC instead of synthetic chemicals. Furthermore, no heating is required in the treatment. This concludes the promising future of biomaterials as an effective coagulant and adsorbent for emulsion waste treatment.

5.2 Limitations & Recommendations

Analysis of cost on the production of these effective RSSAC has not been carried out but as the abundant agricultural waste in Malaysia, rubber seeds can be obtained locally and is expected to be economical except the fact that the rubber seeds harvesting is seasonal. However, the seeds can be collected and stored in advance for productions from time to time yearly.

The presence of residual RSSAC in the treated wastewater is undesirable. The fine RSSAC may be reproduced at a larger size distribution than 162 μm because it is hard to trap, filter and recover the used RSSAC. However, the treated wastewater can be further processed by using membrane ultrafiltration to remove them. Ultrafiltration is able to trap very fine particles and produce an excellent clarity of water (Peters et al., 2004). Also, the colour content in the treated wastewater indicates the presence of heavy metals and can be further treated to improve filtrate clarity.

RSS may be further explored into producing activated carbon by other means of activation rather than chemical method and also may be further explored to treat and adsorb other types of substance such as dyes, heavy metals and other impurities.

There were slight difficulties with the amount of emulsion waste at the beginning stage of the research work. Limited emulsion waste leads to repetition in experiment since the wastes collected were from different machines every time. It is recommended to collect generous amount of emulsion waste prior laboratory works to save time and cost.

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APPENDICES

A1: Graphics

Preparation of rubber seed shell powder



Fresh rubber seeds



Cracking



Washing



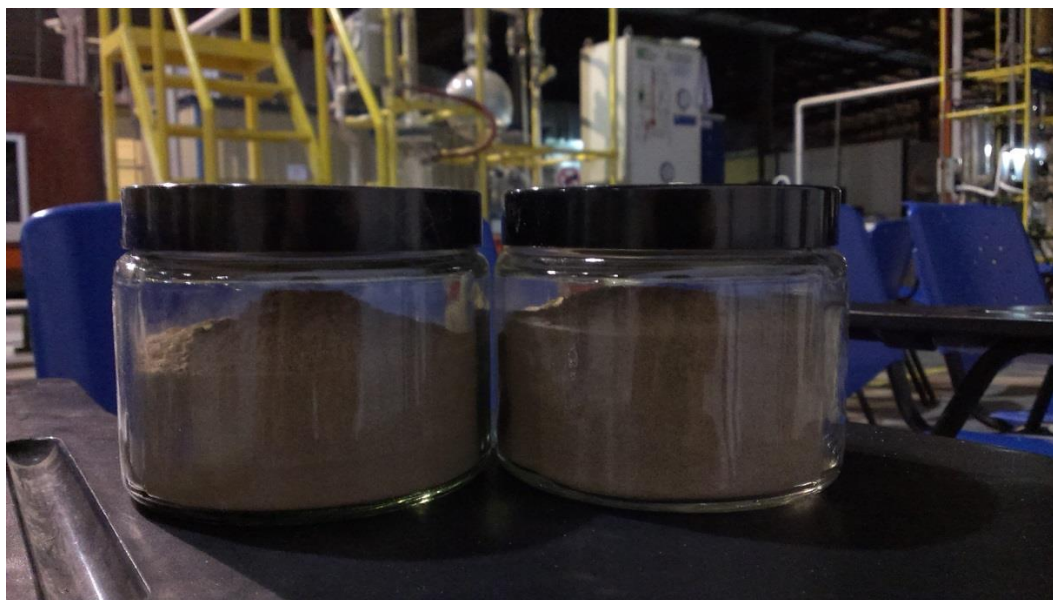
Sun drying



Pulverising



Sieving



Rubber seed shell powder

Carbonization of rubber seed shell powder



Impregnation with NaOH

Carbonization with N₂ flow



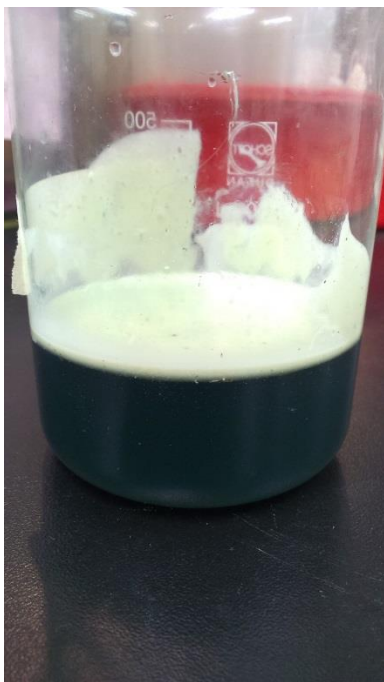
Produced activated carbon

Hot distilled water washing → Oven dried



Produced rubber seed shell activated carbon (RSSAC)

Emulsified wastewater



(A)

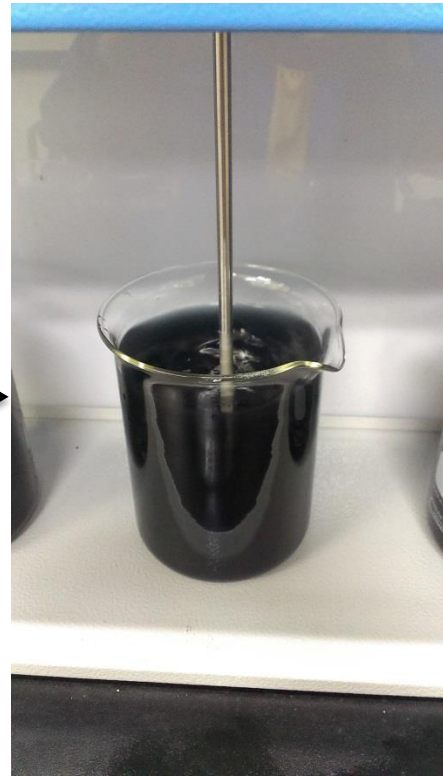


(B)

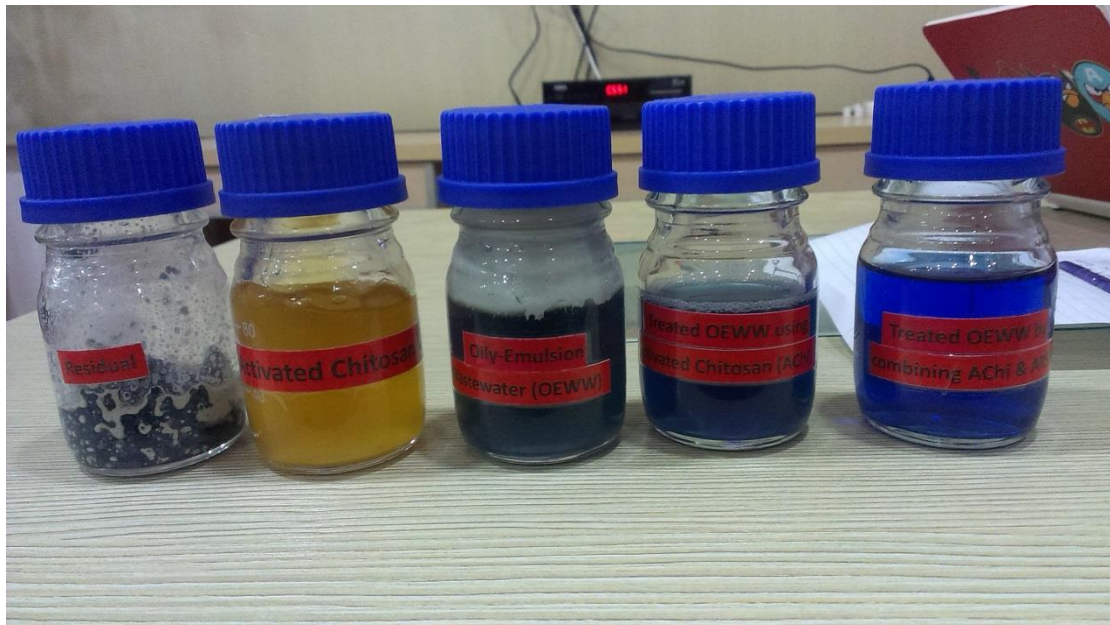
Emulsion waste treatment



Coagulation with chitosan



Adsorption with RSSAC



From left: Waste residual, activated chitosan, raw emulsion wastewater, treated emulsion wastewater with chitosan, treated emulsion wastewater with chitosan + RSSAC.

A2: Raw data

Effect of mixing time

Table 1: O&G after chitosan treatment

Mixing time (min)	Weight of flask before (A), (g)	Weight of flask after (B), (g)	Weight of residue (B - A), (g)	O&G $\left(\frac{B-A}{0.350} \times 1000\right)$, $\left(\frac{mg}{L}\right)$
20	101.44	102.50	1.06	3027.1
25	101.44	102.32	0.88	2514.2
30	101.44	101.75	0.31	884.3
35	101.44	101.80	0.36	1028.0
40	101.44	102.28	0.84	2400.0

Table 2: TSS after chitosan treatment

Mixing time (min)	Weight of filter (A), (mg)	Weight of flask + dried residue (B), (mg)	Net weight (B - A), (g)	TSS $\left(\frac{B-A}{50} \times 1000\right)$, $\left(\frac{mg}{L}\right)$
20	105.0	105.2	0.2	4.0
25	104.0	104.3	0.3	6.0
30	104.4	105.8	1.4	28
35	103.6	103.8	0.2	4.0
40	102.4	103.0	0.6	12.0

Table 3: O&G after chitosan + RSSAC treatment

Mixing time (min)	Weight of flask before (A), (g)	Weight of flask after (B), (g)	Weight of residue (B - A), (g)	O&G $\left(\frac{B-A}{0.200} \times 1000\right)$, $\left(\frac{mg}{L}\right)$
20	98.03	98.37	0.34	1700.0
25	98.03	98.27	0.24	1200.0
30	98.03	98.40	0.37	1850.0
35	98.03	98.23	0.20	1000.0
40	98.03	98.20	0.17	350.0

Table 4: TSS after chitosan + RSSAC treatment

Mixing time (min)	Weight of filter (A), (mg)	Weight of flask + dried residue (B), (mg)	Net weight (B - A), (g)	TSS $\left(\frac{B-A}{50} \times 1000\right), \left(\frac{mg}{L}\right)$
20	103.4	104.4	1.0	20.0
25	104.5	105.7	1.2	24.0
30	103.3	104.7	1.4	28.0
35	105.2	106.7	1.5	30.0
40	104.0	105.4	1.4	28.0

Effect of dosage

Table 1: O&G after chitosan treatment

Dosage of chitosan (wt. %)	Weight of flask before (A), (g)	Weight of flask after (B), (g)	Weight of residue (B - A), (g)	O&G $\left(\frac{B-A}{0.350} \times 1000\right), \left(\frac{mg}{L}\right)$
3.2	101.4	102.25	0.85	2427.1
3.6	101.4	102.36	0.96	2741.4
4.0	101.4	101.82	0.42	1198.6
4.4	101.4	101.71	0.31	884.29
4.8	101.4	102.09	0.69	1998.6

Table 2: TSS after chitosan treatment

Dosage of chitosan (wt. %)	Weight of filter (A), (mg)	Weight of flask + dried residue (B), (mg)	Net weight (B - A), (g)	TSS $\left(\frac{B-A}{50} \times 1000\right), \left(\frac{mg}{L}\right)$
3.2	105.1	105.3	0.2	4
3.6	104.3	106.1	1.8	35
4.0	102.8	104.3	1.5	30
4.4	104.6	106.0	1.4	28
4.8	104.4	104.8	0.4	8

Table 3: O&G after chitosan + RSSAC treatment

Dosage of RSSAC (wt. %)	Weight of flask before (A), (g)	Weight of flask after (B), (g)	Weight of residue (B - A), (g)	O&G $\left(\frac{B-A}{0.200} \times 1000\right), \left(\frac{mg}{L}\right)$
0.2	100.57	100.92	0.35	1750.0
0.4	100.57	100.85	0.28	1400.0
0.6	100.57	100.88	0.31	1550.0
0.8	100.57	100.89	0.32	1600.0
1.0	100.57	100.74	0.17	850.0

Table 4: TSS after chitosan + RSSAC treatment

Dosage of RSSAC (wt. %)	Weight of filter (A), (mg)	Weight of flask + dried residue (B), (mg)	Net weight (B - A), (g)	TSS $\left(\frac{B-A}{50} \times 1000\right), \left(\frac{mg}{L}\right)$
0.2	103.4	106.7	3.3	66
0.4	105.0	105.5	0.5	10
0.6	105.2	106.6	1.4	28
0.8	105.5	106.7	1.2	24
1.0	105.5	107.0	1.5	30

Results of raw emulsified wastewater

Table 1: Results of raw emulsified wastewater

No	Parameter	Unit	Value
1	O&G	mg/L	3657.1
2	TSS	mg/L	More Than 750
3	Turbidity	mg/L	70
4	pH	mg/L	9.71