DEVELOPMENT OF EMULSIFIED WASTEWATER TREATMENT SYSTEM

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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 $S_{BET}$ (19.2403m$^2$/g) at 650°C compared to $S_{BET}$ (0.9482m$^2$/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 pemprosesan logam sebagai bahan penyejuk dan minyak pelincir. Sisa emulsi akan dibuang selepas digunakan. Sisa ini perlu dirawat bagi memenuhi had standard sebelum dilepaskan ke lauan 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 dilakukan. 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, dikerisi, diisar, diayak dan diaktifkan dengan NaOH sebelum proses karbonisasi untuk menghasilkan RSSAC. Karbonisasi dapat meningkatkan S\textsubscript{BET} sehingga 20 kali ganda. Keputusan menunjukkan bacaan tertinggi S\textsubscript{BET}(19.2403m\textsuperscript{2}/g) pada 650°C berbanding S\textsubscript{BET}(0.9482 m\textsuperscript{2}/g) sebelum proses karbonisasi. Karbonisasi berkesan untuk menggalakkan pembentukan liang baru. Walau bagaimanapun, nilai S\textsubscript{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. Kesaran 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 memerangi sisa RSSAC. Selain itu, warna yang menunjukkan kehadiran logam berat boleh dirawat dengan lebih lanjut untuk memperbaiki kejelasan hasil turas. 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.
# TABLE OF CONTENTS

SUPERVISORS’ DECLARATION .................................................................................. IV
STUDENT’S DECLARATION .................................................................................... V
Dedication ................................................................................................................ VI
ACKNOWLEDGEMENT .............................................................................................. VII
ABSTRACT ................................................................................................................ VIII
ABSTRAK .................................................................................................................. IX
LIST OF FIGURES ...................................................................................................... XII
LIST OF TABLES ........................................................................................................ XIII
LIST OF ABBREVIATIONS ....................................................................................... XIV

1.0 INTRODUCTION ................................................................................................. 1
  1.1 Motivation and brief review .............................................................................. 1
  1.2 Problem Statement ........................................................................................... 5
  1.3 Research Objective .......................................................................................... 6
  1.4 Research Scope .................................................................................................. 6

2.0 LITERATURE REVIEW ...................................................................................... 7
  2.1 Chapter Overview ............................................................................................. 7
  2.2 Emulsion ............................................................................................................ 7
  2.3 Treatment Method: Coagulation and Flocculation .......................................... 9
      2.3.1 Mixing Theory .......................................................................................... 11
      2.3.2 Coagulant Aids ....................................................................................... 11
      2.3.3 Coagulant Selection ................................................................................ 11
      2.3.4 Chitosan as Coagulant ............................................................................ 13
  2.4 Treatment Method: Adsorption ....................................................................... 16
      2.4.1 Adsorption Theory and Rationality of Adsorption Method ...................... 16
      2.4.2 Potential Adsorbents .............................................................................. 18
      2.4.3 Commercial Adsorbents ........................................................................ 19
      2.4.4 Low-cost Agricultural Waste as Substitute Adsorbents ......................... 22
      2.4.5 Rubber seed shell as Adsorbent ............................................................. 23
  2.5 Treatment of Industrial Wastewaters .............................................................. 26
  2.6 Conclusion ......................................................................................................... 26
LIST OF FIGURES

Figure 1 - 1: Parameter limits of effluent of Standards A and B. Adapted from “Environmental Quality (Sewage and Industrial Effluents) Regulations 1979”, p. 107 .......... 3

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................................................. 14

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 Ekebefe, et al., 2012, Arabian Journal of Chemistry, 1878-5352. .......................... 25

Figure 3 - 1: Activation of chitosan........................................................................................................................................... 29
Figure 3 - 2: Preparation of RSSAC....................................................................................................................................... 29
Figure 3 - 3: Schematic diagram of treatment of emulsified wastewater .......................................................... 31

Figure 4 - 1: Effect of temperature on the BET surface area of RSSAC. Carbonization time = 120 min.............................................................. 34

Figure 4 - 2: Effect of mixing time on the O&G removal % ................................................................. 40
Figure 4 - 3: Effect of dosage on the O&G removal % ................................................................. 40
Figure 4 - 4: Effect of mixing time on the TSS removal % ............................................................. 43
Figure 4 - 5: Effect of dosage on the TSS removal % ................................................................. 43
Figure 4 - 6: Effect of mixing time on the turbidity removal % ..................................................... 46
Figure 4 - 7: Effect of dosage on the turbidity removal % ............................................................. 46
Figure 4 - 8: Effect of mixing time on the pH value .............................................................................. 49
Figure 4 - 9: Effect of dosage on the pH value .............................................................................. 49
LIST OF TABLES

Table 2 - 1: Parameter values of the raw emulsified wastewater ........................................ 8

Table 3 - 1: Significance of parameters monitored in this research ........................................ 28
Table 3 - 2: Summarized experimental analysis method .......................................................... 32

Table 4 - 1: Results of produced activated RSS and RSSAC .................................................. 33
Table 4 - 2: Characteristics of raw emulsified wastewater in comparison with the parameter limits of effluent of standards A and B. ................................................................. 35
Table 4 - 3: Physical properties of raw emulsified wastewater ............................................. 37
Table 4 - 4: Effect of mixing time and dosage on the O&G removal at initial oil concentration of 3657.1mg/L ................................................................. 39
Table 4 - 5: Effect of mixing time and dosage on the TSS removal at initial TSS concentration of 750mg/L ................................................................. 42
Table 4 - 6: Effect of mixing time and dosage on the turbidity removal at initial turbidity level of 70mg/L ........................................................................... 45
Table 4 - 7: Effect of mixing time and dosage on the pH value ............................................ 48
Table 4 - 8: Summary of produced optimum results .............................................................. 51
**LIST OF ABBREVIATIONS**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOD</td>
<td>Biochemical oxygen demand</td>
</tr>
<tr>
<td>CAC</td>
<td>Commercial activated carbon</td>
</tr>
<tr>
<td>CNC</td>
<td>Computer numerical control machine</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical oxygen demand</td>
</tr>
<tr>
<td>DOE</td>
<td>Design of experiment</td>
</tr>
<tr>
<td>GAC</td>
<td>Granular activated carbon</td>
</tr>
<tr>
<td>MTZ</td>
<td>Mass transfer zone</td>
</tr>
<tr>
<td>NOM</td>
<td>Natural organic matter</td>
</tr>
<tr>
<td>O&amp;G</td>
<td>Oil and grease</td>
</tr>
<tr>
<td>O/W</td>
<td>Oil in water</td>
</tr>
<tr>
<td>PAC</td>
<td>Powdered activated carbon</td>
</tr>
<tr>
<td>RSCC</td>
<td>Rubber seed coat carbon</td>
</tr>
<tr>
<td>RSS</td>
<td>Rubber seed shell</td>
</tr>
<tr>
<td>RSSAC</td>
<td>Rubber seed shell activated carbon</td>
</tr>
<tr>
<td>SCD</td>
<td>Streaming current detector</td>
</tr>
<tr>
<td>TSS</td>
<td>Total suspended solids</td>
</tr>
<tr>
<td>W/O</td>
<td>Water in oil</td>
</tr>
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</table>
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.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Standard A</th>
<th>Standard B</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) Temperature</td>
<td>°C</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>(ii) pH value</td>
<td>-</td>
<td>6.0 - 9.0</td>
<td>5.5 - 9.0</td>
</tr>
<tr>
<td>(iii) BOD at 20°C</td>
<td>mg/l</td>
<td>20</td>
<td>50</td>
</tr>
<tr>
<td>(iv) COD</td>
<td>mg/l</td>
<td>50</td>
<td>100</td>
</tr>
<tr>
<td>(v) Suspended Solids</td>
<td>mg/l</td>
<td>50</td>
<td>100</td>
</tr>
<tr>
<td>(vi) Mercury</td>
<td>mg/l</td>
<td>0.005</td>
<td>0.05</td>
</tr>
<tr>
<td>(vii) Cadmium</td>
<td>mg/l</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>(viii) Chromium, Hexavalent</td>
<td>mg/l</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>(ix) Arsenic</td>
<td>mg/l</td>
<td>0.05</td>
<td>0.10</td>
</tr>
<tr>
<td>(x) Cyanide</td>
<td>mg/l</td>
<td>0.05</td>
<td>0.10</td>
</tr>
<tr>
<td>(xi) Lead</td>
<td>mg/l</td>
<td>0.10</td>
<td>0.5</td>
</tr>
<tr>
<td>(xii) Chromium Trivalent</td>
<td>mg/l</td>
<td>0.20</td>
<td>1.0</td>
</tr>
<tr>
<td>(xiii) Copper</td>
<td>mg/l</td>
<td>0.20</td>
<td>1.0</td>
</tr>
<tr>
<td>(xiv) Manganese</td>
<td>mg/l</td>
<td>0.20</td>
<td>1.0</td>
</tr>
<tr>
<td>(xv) Nickel</td>
<td>mg/l</td>
<td>0.20</td>
<td>1.0</td>
</tr>
<tr>
<td>(xvi) Tin</td>
<td>mg/l</td>
<td>0.20</td>
<td>1.0</td>
</tr>
<tr>
<td>(xvii) Zinc</td>
<td>mg/l</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>(xviii) Boron</td>
<td>mg/l</td>
<td>1.0</td>
<td>4.0</td>
</tr>
<tr>
<td>(xix) Iron (Fe)</td>
<td>mg/l</td>
<td>1.0</td>
<td>5.0</td>
</tr>
<tr>
<td>(xx) Phenol</td>
<td>mg/l</td>
<td>0.001</td>
<td>1.0</td>
</tr>
<tr>
<td>(xxi) Free Chlorine</td>
<td>mg/l</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td>(xxii) Sulphide</td>
<td>mg/l</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>(xxiii) Oil and Grease</td>
<td>mg/l</td>
<td>Not Detectable</td>
<td>10.0</td>
</tr>
</tbody>
</table>
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 biosorbents 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.

<table>
<thead>
<tr>
<th>No</th>
<th>Parameter</th>
<th>Results</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Density</td>
<td>1.001</td>
<td>g/cm³</td>
</tr>
<tr>
<td>2</td>
<td>Turbidity</td>
<td>70</td>
<td>NTU</td>
</tr>
<tr>
<td>3</td>
<td>pH</td>
<td>9.71 @ 24.5°C</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>TSS</td>
<td>More Than 750</td>
<td>mg/L</td>
</tr>
<tr>
<td>5</td>
<td>O&amp;G</td>
<td>More Than 100</td>
<td>mg/L</td>
</tr>
<tr>
<td>6</td>
<td>Viscosity</td>
<td>132.6</td>
<td>cP</td>
</tr>
</tbody>
</table>
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→4)-linked 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.

![Structures of cellulose, chitin and chitosan.](image)

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, cosmeceuticals 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,
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 if 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