UNIVERSITI PUTRA MALAYSIA

APPLICATION OF ESTERIFIED SAGO BARK FOR REMOVAL OF OIL FROM PALM OIL MILL EFFLUENT

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By

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Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia in Fulfilment of the Requirements for the Degree of Doctor of Philosophy
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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

APPLICATION OF ESTERIFIED SAGO BARK FOR REMOVAL OF OIL FROM PALM OIL MILL EFFLUENT

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November 2014

Chair: Professor Luqman Chuah Abdullah, PhD
Faculty: Engineering

Removal of emulsified oil in palm oil mill effluent (POME) is a challenge to palm oil industries. The aim of the present study was to develop a hydrophobic oil sorbent by incorporating fatty acid derivatives, namely stearic acid, on sago bark (SB) network via esterification process. The effect of esterification parameters such as the SB to stearic acid (SA) ratio (SB:SA), the amount of catalyst and the refluxing time on the oil removal efficiency of ESB and the optimization study were conducted via surface response methodology (RSM). The oil removal efficiency of SB and ESB in POME was also studied at different adsorption conditions in batch experiments. Artificial neural network (ANN) modelling was applied to model the column oil adsorption process.

Chemical modification of SB has been successfully carried out via esterification with SA to afford ESB, the oil sorbent of high hydrophobicity and high oil removal efficiency. The esterification has successfully increased the hydrophobicity of SB by 42.2% and the oil removal efficiency in POME by 50.2%. The ESB produced at the optimum operating condition of SB:SA 1:1, 15% catalyst, and 8 h refluxing time gave the highest oil removal efficiency in POME (95.52%). The two most dominant influencing factors for ESB preparation were SB:SA and refluxing time.

The batch oil adsorption study showed that the ESB exhibits better oil removal efficiency compared to SB in all studied conditions, namely adsorbent dosage, contact time, temperature and pH. Overall, the oil removal efficiency of both SB and ESB increased with increasing sorbent dosage and contact time. On the other hand, the oil removal efficiency of both SB and ESB decreased with the increasing temperature. Acidic pH was favorable pH condition for high oil removal efficiency. Overall, results showed a good correlation ($R^2 > 9.5$) between experimental data and the intra-particle diffusion model for both SB and ESB. Results also showed that adsorption of oil in POME using SB was best described by Freundlich isotherm (R^2=0.998), indicating heterolayer adsorption of oil on SB. The adsorption of oil in POME using ESB was better represented using Langmuir isotherm (R^2=0.992), indicating a monolayer adsorption of oil onto the ESB surface.

It is also evident from the study that ESB afforded good oil removal efficiency in deep bed filtration system. The ANN data showed that SB and ESB were found to remove oil from POME up to 59.12% and 89.79%, respectively in column system. The data means that after deep bed filtration of typical POME with initial oil concentration of 4000 mg/l using ESB, the treated POME is estimated to have 409 mg/l oil and grease content. ANN model was found to fit well with the experimental data with $R^2 > 0.95$ for both training and testing data of SB and ESB. ANN study also indicated that all studied parameters are effective parameters in the sequence of temperature (30.09%) > pH (26.8%) > bed height (26.73% > flow rate (16.38%). The result revealed that the Thomas model and Yoon & Nelson model did not represented the experimental data very well. On the other hand, the column oil adsorption from POME using ESB can be excellently described by the intra-particle diffusion model. A multi-linearity plot of intra-particle diffusion model indicated the occurrence of three stages of adsorption during the experiment. Good oil removal efficiency and environmental friendliness make ESB a viable choice for use as bed material of a deep bed filter system for emulsified oil removal from POME. The importance of these research findings to advance the emulsified oil removal technology will hopefully find good use in the oil processing industry. The findings of this research will provide new insights to the emulsified oil removal technology.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

APLIKASI KULIT POKOK SAGU TERESTERIFIKASI UNTUK PENYINGKIRAN MINYAK DARI EFLUEN KILANG MINYAK SAWIT

Oleh

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November 2014

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Penyingkiran minyak teremulsi dalam efluen kilang sawit (POME) adalah satu proses yang mencabar. Tujuan kajian ini adalah untuk menghasilkan penjerap minyak yang hidrofobik dengan menggabungkan derivatif asid lemak iaitu asid stearik, melalui proses pengesteran. Kesan parameter pengesteran iaitu nisbah SB kepada asid stearik (SA) (SB:SA), jumlah pemangkin dan tempoh refluks terhadap kecekapan penyingkiran minyak, serta pengoptimuman parameter pengesteran telah dijalankan menggunakan kaedah tindak balas permukaan (RSM). Kecekapan penyingkiran minyak oleh SB dan ESB di dalam POME juga dikaji pada keadaan penyerapan yang berbeza dalam eksperimen kumpulan. Model rangkaian neural buatan (ANN) telah digunakan untuk permodelan proses penjerapan minyak.

Pengubahsuaian kimia secara esterifikasi telah berjaya meningkatkan sifat-sifat penyingkiran minyak SB. ESB mempunyai hidrofobisiti sebanyak 42.2 % lebih tinggi berbanding dengan SB, dan kecekapan penyingkiran minyak di dalam POME adalah 50.2 % lebih tinggi daripada SB. ESB yang dihasilkan pada keadaan operasi SB:SA 1:1, 15% pemangkin , dan 8 jam tempoh refluks memberikan kecekapan penyingkiran minyak di dalam POME yang tertinggi (95.52%). Dua faktor yang paling dominan yang mempengaruhi penyediaan ESB adalah SB:SA dan tempoh refluks. Pencirian fizikokimia ke atas penjerap menunjukkan bahawa ESB mempunyai hidrofobisiti, keapungan, morfologi permukaan dan isipadu liang yang lebih baik berbanding SB.

Kajian penyerapan minyak berkumpulan menunjukkan bahawa ESB memberikan kecekapan penyingkiran minyak yang lebih baik berbanding SB di dalam semua keadaan yang dikaji iaitu dos penjerap, masa penjerapan, suhu dan pH. Umumnya, kecekapan penyingkiran minyak oleh SB dan ESB meningkat apabila dos penjerap dan masa penjerapan meningkat. Namun demikian, kecekapan penyingkiran minyak menurun apabila suhu meningkat. pH berasid adalah lebih baik untuk kecekapan penyingkiran minyak yang tinggi. Secara keseluruhan, keputusan menunjukkan korelasi yang baik (R^2 > 9.5) di antara data eksperimen dengan model difusi intra-zarah untuk SB dan ESB.

Keputusan juga menunjukkan bahawa penjerapan minyak dari POME menggunakan SB dapat diwakili oleh isotherm Freundlich (R^2=0.998) yang menunjukkan penjerapan minyak secara berlapis-lapis pada SB. Penjerapan minyak oleh ESB dapat diwakili oleh isotherm Langmuir (R^2=0.992) yang mewakili penjerapan satu lapisan ke atas permukaan ESB.

Kajian ini juga membuktikan bahawa ESB mempunyai kecekapan penyingkiran minyak yang baik di dalam sistem penapisan. Data ANN menunjukkan bahawa SB dan ESB masing-masing didapati menyingkirkan minyak dari POME sehingga 59.12 % dan 89.79 %. Ini menunjukkan bahawa, setelah POME yang mempunyai kepekatan minyak sebanyak 4000 mg/L melalui penapisan menggunakan ESB, POME yang terawatt dijangka mempunyai kepekatan minyak sebanyak 409 mg/L. Model ANN juga didapati sepadan dengan data eksperimen dengan R^2> 0.95 bagi kedua-dua data latihan dan data ujian untuk SB dan ESB. Kajian ANN menunjukkan bahawa semua parameter yang dikaji adalah berkesan mengikut turutan: suhu (30.09%) > pH (26.8%) > ketinggian lapisan (26.73%) > kadar aliran (16.38%). Keputusan menunjukkan bahawa data eksperimen tidak diwakili dnegan baik oleh model Thomas dan model Yoon & Nelson. Sebaliknya, penjerapan minyak secara kolum dapat diwakili dengan baik oleh model difusi intra-zarah. Beberapa plot linear pada model difusi ini menunjukkan bahawa penjerapan secara kolum berlaku dalam tiga langkah. Kesimpulannya, kecekapan penyingkiran minyak yang baik dan sifat mesra alam ESB menjadikannya pilihan yang sesuai sebagai bahan penapis dalam sistem penapisan POME untuk penyingkiran minyak. Adalah diharapkan bahawa penemuan kajian ini memberi sumbangan yang penting bagi memajukan teknologi penyingkiran minyak teremulsi teknologi penyingkiran minyak. Hasil kajian ini akan memberi maklumat baru untuk teknologi penyingkiran minyak teremulsi.

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I certify that a Thesis Examination Committee has met on 6th November 2014 to conduct the final examination of Rafeah binti Wahi on her thesis entitled "Application of esterified sago bark for removal of oil from palm oil mill effluent" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee are as follows:

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LIST OF ABBREVIATIONS

ANN	Artificial neural network
BET	Brunaer, Emmet and Taller
DOE	Department of Environment
ESB	Esterified sago bark
FTIR	Fourier Transform Infra Red
POME	Palm oil mill effluent
RMSE	Root mean square error
RSM	Response surface methodology
SA	Stearic acid
SB	Sago bark
SEM	Scanning electron microscope

CHAPTER 1

INTRODUCTION

1.1 Background of study

Oily wastewater is becoming one of the environmental concerns nowadays. The seriousness of oil pollution problem comes in sync with the expansion of oil exploration and production activities, as well as industrial growth around the world. For instance, annual worldwide use of petroleum-based products and vegetables oils are approximated to exceed 100 and 92 million tonnes, respectively (USDA, 2012; Abdullah et al., 2010). It is estimated that between 2000 and 2011 alone, 224,000 tonnes of petroleum oil polluted the worldwide marine due to oil tanker spill (ITOPF, 2011).

Oil in wastewater can be found in various forms such as fats, lubricants, cutting oils, heavy hydrocarbons, and light hydrocarbons (Srinivasan and Viraraghavan, 2008). These oils can be further divided into two categories, namely free and emulsified oils. The free oil fraction of the wastewater is easier to treat by physical techniques such as gravity separation and skimming (Aranđelovic et al., 2009; Ahmad et al., 2006). In contrast, emulsions or the oil droplets dispersed in water phase, are more difficult to treat due to their high stability in aqueous phase (Angelova et al., 2011; Annunciado et al., 2005).

Oily wastewater originates from various sources such as the food, vegetable oil, metal, textile and leather industries, oil and gas production, domestic sewage, kitchens, and vehicles (Santander et al., 2002). Environmental contamination occurs during oil and gas production as oil is transferred to the environment by transportation, refining, and use of oil (Ibrahim et al., 2010; Banerjee et al., 2006). It is estimated that the total annual oil pollution through transportation of petroleum hydrocarbons alone could reach up to 10 million metric tonnes (Banerjee et al., 2006). Meanwhile, oily wastewater concentration generated by industrial activities could reach as high as 40,000 mg/l (Arcadio and Gregoria, 2003). Oil is usually removed from wastewater prior to discharge to the environment to meet the maximum allowable limit of oil and grease in water as required by local enforcing agency. However, oily wastewater from kitchens and small enterprises is commonly discharged without any prior treatment and hard to control.

Unlike other water contaminants, not all countries have set maximum allowable limit for oil and grease in water. For example, the maximum limit for oil and grease in drinking water is not mentioned in World Health Organisation (WHO) drinking water guidelines (2011) (WHO, 2011) and European Communities (Drinking Water) (No. 2) Regulations 2007 (European Communities (Drinking Water) (No. 2) Regulations, 2007). The United States Environmental Protection Agency (USEPA) limits oil and grease content in drinking water to 0.3 mg/l (Ahmad et al., 2006). In Malaysia, the maximum allowable limit set by the Department of Environment for oil and grease in water is 50 mg/l.

One of the main sources of industrial oily wastewater in Malaysia is the palm oil mill effluent (POME). POME is generated at significant level as a by-product during palm oil processing. It was recorded that in year 2008 alone, at least 44 million tonnes of POME was generated in Malaysia (Wu et al., 2010). The oil concentration in POME ranges between 4000-8000 mg/l (Ngarmkam et al., 2011; Ahmad et al., 2006).

Most palm oil mills use ponding system to treat POME as it is more convenient and has low operating cost. However, ponding system requires long treatment time and large area to treat POME (Wu et al., 2010). Besides, the Malaysian Department of Environment (DOE) has set 50mg/l as the maximum allowable limit for oil and grease content in effluent to be discharged in waterways. With oil and grease content of 4000-8000 mg/l in POME, sometimes the ponding system fails to produce treated effluent that meets the DOE standard (Chin et al., 1996). Thus, it is crucial for the palm oil industries to adapt an efficient treatment for oil removal.

In view of industrial oily wastewater like POME, many technologies have been suggested for oil removal from water. For example, treatment of oily wastewater by micro and ultrafiltration often give the highest oil removal efficiency compared to other methods. However, they are not suitable for treating wastewater with high solid content due to risk of premature membrane fouling, and require high initial and operating cost (Yi et al., 2011; Wu et al., 2007). Other treatments like coagulation, flotation and biological treatment are either expensive, has complex operation or required highly skilled operators. Among all oil removal technologies, adsorption is the most preferred method due to its feasibility and effectiveness, provided appropriate sorbent is used. Natural fibres are potential source of natural sorbent for removal of oil from POME.

Raw natural sorbents generally has excellent adsorption capacity, comparable density with synthetic sorbent, chemical free and highly biodegradable (Wang et al., 2012; Rajaković-Ognjanović et al., 2008; Annunciado et al., 2005). Numerous natural fibers have been used as oil sorbent such as rice husk (Ali et al., 2012), kapok (Abdullah et al., 2010), barley straw (Ibrahim et al., 2010), sugarcane baggase (Said et al., 2009), sawdust (Cambiella et al., 2006) and grass (Suni et al., 2004). These natural sorbents comprise of cellulose and lignin, which is known responsible for the oil adsorption (Quek et al., 1998).

Despite their advantages, many natural fibers suffer low hydrophobicity and buoyancy, and therefore only suitable for oil removal in the absence of water (Ali et al., 2012). In response, many studies have been conducted on methods to improve the hydrophobicity of natural fibers. For instance, hydrophobization was conducted by means of alkalization (Abdullah et al., 2010), chloroform treatment (Likon et al., 2012; Abdullah et al., 2010), acetylation (Ren et al., 2007; Adebajo and Frost, 2004), salt treatment (Wang et al., 2012), surfactant treatment (Ibrahim et al., 2010; Ibrahim et al., 2009), combination of chemical-biotechnological treatment (Garcia-Ubasart et al., 2012) and esterification (Said et al., 2009; Banerjee et al., 2006).

Sago, known scientifically as *Metroxylon sagu* Rottboll comes from genus metroxylon and family palmae (Singhal et al., 2008). Sago palm is commonly found in tropical lowland forest and freshwater swamps. In 2009, nearly 59,000 hectares land of Sarawak is planted with sago (Department of Agriculture Sarawak, 2009a). Sarawak is currently one of the world largest exporters of sago products, with approximately

43,000 tonnes sago starch exported to several countries annually (Department of Agriculture Sarawak, 2009b; Department of Agriculture Sarawak, 2009c).

During sago processing, vast amount of solid and liquid waste are generated – most are left unutilized or improperly disposed off. For every tonne of sago flour produced, about 0.75 tonnes of sago bark (SB) are generated (Vikineswary et al., 1994). Thus, SB is a potential source of natural fiber for oil removal with estimated generation of SB in Sarawak of more than 32,000 tonnes/yr (Appendix A).

Current practice in managing the overabundant SB could cause a serious threat to the environment. Only less than 5% of the bark is used as fuel in sago processing mill due to the corrosion problem caused by SB (Chew et al., 1999). Eliminating the SB through open and controlled burning, could either cause air pollution or furnace chimney corrosion. Because of its woody nature, SB degrades slowly. Dumping SB into nearby rivers is unacceptable as it could cause the rivers to become shallow. On the other hand, leaving tonnes of SB to naturally degrade consumes space and time, and could cause unpleasant odour and view. With regards to the above-mentioned problem, there is an urgent need to find ways to systematically utilize SB.

Like other natural sorbents, SB comprises of cellulose and lignin, which is known responsible for oil adsorption (Quek et al., 1998; Said et al., 2009; Singhal et al., 2008). Previous study by (Noh et al., 2012) showed that SB posses good oil adsorption capacity on engine oil, which ranges from 3.2-3.3 g oil/g SB at 40 min treatment in dry, wet (static) and wet (dynamic) systems. At the same time, it was observed that the SB has tendency to sink upon prolonged stay in water. Moreover, the water uptake is considerably high (3.3 g water/g SB), suggesting that SB is only suitable for removal of oil in dry system. Thus, in this study, hydrophobization of SB through chemical treatment was suggested to overcome the problem of poor buoyancy and high water uptake in SB.

Based on the literature precedent and preliminary findings, it was envisaged that chemical modification of SB via esterification with fatty acid derivatives has the capability to remove of oil from wastewater (Said et al., 2009; Banerjee et al., 2006). POME was selected as a case study of wastewater containing oil. Effect of various experimental conditions such as sorbent dosage, contact time and initial concentration on oil removal efficiency from POME was also investigated. Finally, model study was conducted by applying Artificial Neural Network (ANN) on the column oil adsorption data.

1.2 Problem statement and justification of study

Many technologies have been suggested for oil removal from POME, such as ponding system, micro and ultrafiltration, coagulation, flotation and biological treatment. However, the technologies are either inefficient, time consuming, expensive, complex in operation or required highly skilled operators. Adsorption is the most preferred method over the previously mentioned technologies due to its feasibility and effectiveness, provided an appropriate sorbent is used. Utilizing the locally abundant agricultural waste such as SB seems to be a potential alternative to obtain a low cost sorbent for oil removal from POME. However, previous study reveals that like many other natural oil sorbent, raw SB has significant water uptake capacity and therefore is not suitable for oil removal in aqueous environment.

Previous studies by Said et al. (2009) and Banerjee et al. (2006) on the esterification of biomass for oil removal used a different types of biomass, esterification procedure, catalyst and solvent. The oil adsorption tests were conducted using different type of oil. The previous study by Said et al. (2009) was performed on the raw bagasse and pulp, whereby these materials were mixed with stearic acid, basic compounds, and water at room temperature for 2 h. Oil adsorption test was conducted using motor oil. However, the limitation of adsorbent produced from this study is that, the stearic acid was only grafted onto the adsorbent surface, not incorporated. Thus, there is a tendency of leaching of stearic acid from the adsorbent produced. Meanwhile, in previous study by Banerjee et al. (2006) the biomass used was sawdust. Esterification of sawdust was conducted using various fatty acid/vegetable oil in n-hexane, H_2SO_4 at 65 °C. The esterification process has increased the oil adsorption capacity of esterified sawdust on crude oil. However, the problem with usage of sulphuric acid as a catalyst is the possibility of corrosion caused by the adsorbent produced. In this study, a different approach was used to perform esterification of a different type of biomass, which is SB. SB was esterified using stearic acid, calcium oxide and ethy acetate, and refluxed at 1-8 h (boiling point of ethyl acetate is 77 ºC). The efficiency of ESB for oil removal was tested using POME. Thus, the present study provides data on the potential application of esterification process to improve the oil adsorption properties of SB in aqueous environment studied, such as POME.

1.3 Research objectives

Based on the earlier stated problems, the overall aim of the present study was to evaluate at laboratory scale, the oil adsorption behaviour of SB and esterified SB (ESB) in POME. The specific objectives are:

1. to develop a hydrophobic oil sorbent by incorporating fatty acid derivatives on sago network via esterification using a new approach.
2. to optimize the esterification parameters via response surface methodology (RSM) study.
3. to determine the oil removal efficiency of SB and ESB in POME at different adsorption condition in batch system.
4. to apply artificial neural network (ANN) to model the column oil removal from POME by SB and ESB.

1.4 Scope of work

The target of this study was to investigate several aspects of oil removal from POME using SB and ESB in order to better understand the factors that limit the preparation of ESB and oil adsorption using ESB. The study was conducted within the following scope of work:

First, in this study, esterification process was conducted at lab scale using RSM experimental design, whereby each experimental run has a unique combination of esterification parameters. The RSM approach is in contrast with conventional one-variable-at-a-time (OVAT) experiments, whereby only one parameter is studied in an experimental run with other parameters kept constant. Therefore, this fact must be taken into consideration during interpretation of results. Second, the batch adsorption experiments were conducted at lab scale using ESB with only one size range, which is 0.5 to 1.5 mm. Therefore, no study was conducted on the effect of different ESB size range on the oil adsorption from POME. Third, the column adsorption experiments were conducted at lab scale using ANN experimental design, whereby like RSM, it has a unique combination of oil adsorption parameters in an experimental run. Therefore, while studying the effect of column bed height, POME flow rate, POME temperature and POME pH on adsorption at different value for each of the experimental run, it is important to keep one factor constant. In this study, the volume of POME was kept constant for the sake of using ANN.

1.5 Thesis structure and content

The present thesis consists of six chapters. Chapter 1 provides brief information on the need for an efficient and simple technology for oil removal from POME. Chapter 2 covers the exhaustive review on previous work related to oil removal in water. Chapter 3 describes the modification of SB to yield hydrophobic oil sorbent, ESB via esterification. Chapter 4 presents the removal of emulsified oil from POME at various operating condition in batch adsorption study. Chapter 5 explores the continuous column adsorption study and the application of artificial neural network (ANN) to model the emulsified oil removal process using SB and ESB. Chapter 6 is the conclusions and highlights the most significant results achieved and suggestions for future work.

REFERENCES

Abd Rahman, K. A. A. (2005). Utilizing Sago (Metroxylon spp) Bark Waste for Value Added Products. In H. K. Ryoichi Yamamoto, Yuji Furukawa, Y. U. Patrick Eagan, Hansjoerg Griese, & and K. Aoyama (Eds.), *Fourth International Symposium on Environmentally Conscius Design and Inverse Manufacturing* (pp. 102–106). Tokyo: The Institute of Electrical and Electronics Engineers, Inc. doi:10.1109/ECODIM.2005.1619175

Abd Rahman, K. A. A., & Sundin, N. (2008). Product Design Development : Recycle Strategy for Sago Industries Waste in Malaysia. *Journal of Industrial Design*, *2*(4), 67–76.

Abdollahi, Y., Zakaria, A., Abbasiyannejad, M., Masoumi, H. R. F., Moghaddam, M. G., Matori, K. A., … Keshavarzi, A. (2013). Artificial neural network modeling of p-cresol photodegradation. *Chemistry Central Journal*, *7*(1), 96. doi:10.1186/1752-153X-7-96

Abdullah, M. A., Rahmah, A. U., & Man, Z. (2010). Physicochemical and sorption characteristics of Malaysian Ceiba pentandra (L.) Gaertn. as a natural oil sorbent. *Journal of Hazardous Materials*, *177*(1-3), 683–91. doi:10.1016/j.jhazmat.2009.12.085

Adebajo, M. O., & Frost, R. L. (2004). Acetylation of raw cotton for oil spill cleanup application: an FTIR and 13C MAS NMR spectroscopic investigation. *Spectrochimica Acta. Part A, Molecular and Biomolecular Spectroscopy*, *60*(10), 2315–21. doi:10.1016/j.saa.2003.12.005

Ahmad, A. L., Chong, M. F., Bhatia, S., & Ismail, S. (2006). Drinking water reclamation from palm oil mill effluent (POME) using membrane technology. *Desalination*, *191*(1-3), 35–44. doi:10.1016/j.desal.2005.06.033

Ahmad, A. L., Sumathi, S., & Hameed, B. H. (2005a). Adsorption of residue oil from palm oil mill effluent using powder and flake chitosan: equilibrium and kinetic studies. *Water Research*, *39*(12), 2483–94. doi:10.1016/j.watres.2005.03.035

Ahmad, A. L., Sumathi, S., & Hameed, B. H. (2005b). Residual oil and suspended solid removal using natural adsorbents chitosan, bentonite and activated carbon: A comparative study. *Chemical Engineering Journal*, *108*(1-2), 179–185. doi:10.1016/j.cej.2005.01.016

Ahmad, A. L., Sumathi, S., & Hameed, B. H. (2006). Coagulation of residue oil and suspended solid in palm oil mill effluent by chitosan, alum and PAC. *Chemical Engineering Journal*, *118*(1-2), 99–105. doi:10.1016/j.cej.2006.02.001

Ahmadi, M., Vahabzadeh, F., Bonakdarpour, B., & Mehranian, M. (2006). Empirical modeling of olive oil mill wastewater treatment using loofa-immobilized Phanerochaete chrysosporium. *Process Biochemistry*, *41*(5), 1148–1154. doi:10.1016/j.procbio.2005.12.012

Alam, M. Z., Muyibi, S. a, & Toramae, J. (2007). Statistical optimization of adsorption processes for removal of 2,4-dichlorophenol by activated carbon derived from oil palm empty fruit bunches. *Journal of Environmental Sciences, 19*(6), 674–7. Retrieved from http://www.ncbi.nlm.nih.gov/pubmed/17969639

Ali, N., El-harbawi, M., Jabal, A. A., & Yin, C. (2012). Characteristics and oil sorption effectiveness of kapok fibre , sugarcane bagasse and rice husks : oil removal suitability matrix. *Environmental Technology*, *33*(4), 481–486.

Angelova, D., Uzunov, I., Uzunova, S., Gigova, A., & Minchev, L. (2011). Kinetics of oil and oil products adsorption by carbonized rice husks. *Chemical Engineering Journal*, *172*(1), 306–311. doi:10.1016/j.cej.2011.05.114

Annunciado, T. R., Sydenstricker, T. H. D., & Amico, S. C. (2005). Experimental investigation of various vegetable fibers as sorbent materials for oil spills. *Marine Pollution Bulletin*, *50*(11), 1340–6. doi:10.1016/j.marpolbul.2005.04.043

Aranđelović, D., Jovanović, M., Kovačević, B., Pezo, L., & Jovanović, A. C. A. (2009). Removal of mineral oil and wastewater pollutants using hard coal. *Chemical Industry & Chemical Engineering Quarterly*, *15*(2), 57–62.

Arcadio, P. S., & Gregoria, A. S. (2003). *Physical–Chemical Treatment of Water and Wastewater*. Washington DC: IWA Publishing, CRC Press.

Banerjee, S., Joshi, M., & Jayaram, R. (2006). Treatment of oil spill by sorption technique using fatty acid grafted sawdust. *Chemosphere*, *64*(6), 1026–1031. doi:10.1016/j.chemosphere.2006.01.065

Bansal, S., von Arnim, V., Stegmaier, T., & Planck, H. (2011). Effect of fibrous filter properties on the oil-in-water-emulsion separation and filtration performance. *Journal of Hazardous Materials*, *190*(1-3), 45–50. doi:10.1016/j.jhazmat.2011.01.134

Bhatia, S., Othman, Z., & Ahmad, A. L. (2007). Coagulation–flocculation process for POME treatment using Moringa oleifera seeds extract: Optimization studies. *Chemical Engineering Journal*, *133*(1-3), 205–212. doi:10.1016/j.cej.2007.01.034

Cambiella, A., Ortea, E., Rios, G., Benito, J., Pazos, C., & Coca, J. (2006). Treatment of oil-in-water emulsions: Performance of a sawdust bed filter. *Journal of Hazardous Materials*, *131*(1-3), 195–199. doi:10.1016/j.jhazmat.2005.09.023

Cao, X., Yang, G., Wei, S., & Han, H. (2011). Sorption of heavy oil onto Jiaozhou Bay sediment. *Marine Pollution Bulletin*, *62*(4), 741–6. doi:10.1016/j.marpolbul.2011.01.016

Chew, T., Hassan, A., & Ghazali, M. (1999). Sago (Metroxylon sagu Rottboll), the Forgotten Palm Sago (Metroxylon sagu Rottboll), the Forgotten Palm. *Journal of Sustainable Agriculture, 14*(4), 5–17. doi:10.1300/J064v14n04_03

Chin, K. K., Lee, S. W., & Mohammad, H. H. (1996). A study of palm oil mill effluent treatment using a pond system. *Water Science and Technology*, *34*(11), 119–123.

Chouchene, A., Jeguirim, M., Favre-Reguillon, A., Trouvé, G., Le Buzit, G., Khiari, B., & Zagrouba, F. (2012). Energetic valorisation of olive mill wastewater impregnated on low cost absorbent: Sawdust versus olive solid waste. *Energy*, *39*(1), 74–81. doi:10.1016/j.energy.2011.03.044

Clesceri, L. S., Greenberg, A. E., & Eaton, A. D. (Eds.). (1999). *Standard Methods for the Examination of Water and Wastewater Standard Methods for the Examination of Water and Wastewater* (20th ed.).

Cojocaru, C., Macoveanu, M., & Cretescu, I. (2011). Peat-based sorbents for the removal of oil spills from water surface: Application of artificial neural network modeling. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *384*(1-3), 675–684. doi:10.1016/j.colsurfa.2011.05.036

Crank, J. (1975). The mathematics of diffusion. Clarendon Press, Oxford, 2nd ed. pp91.

Cunha, M. a. E., Neves, R. F., Souza, J. N. S., França, L. F., Araújo, M. E., Brunner, G., & Machado, N. T. (2011). Supercritical adsorption of buriti oil (Mauritia flexuosa Mart.) in γ-alumina: A methodology for the enriching of anti-oxidants. *The Journal of Supercritical Fluids*, 1–11. doi:10.1016/j.supflu.2011.10.021

Da Silva Jr., U. G., de F. Melo, M. a., da Silva, A. F., & de Farias, R. F. (2003). Adsorption of crude oil on anhydrous and hydrophobized vermiculite. *Journal of Colloid and Interface Science*, *260*(2), 302–304. doi:10.1016/S0021-9797(02)00160-1

Department of Agriculture Sarawak. (2009a). Estimated Area of Sago by District 2009. Retrieved March 24, 2012, from http://www.doa.sarawak.gov.my/modules/web/page.php?id=102

Department of Agriculture Sarawak. (2009b). Export of Sago Starch by Country of Destination 2005 – 2009. Retrieved April 13, 2012, from http://www.doa.sarawak.gov.my/modules/web/page.php?id=102

Department of Agriculture Sarawak. (2009c). Export Value of Agricultural Products 2000 – 2009. Retrieved March 24, 2012, from http://www.doa.sarawak.gov.my/modules/web/page.php?id=102

Deschamps, G., Caruel, H., Borredon, M.-E., Bonnin, C., & Vignoles, C. (2003). Oil removal from water by selective sorption on hydrophobic cotton fibers. 1. Study of sorption properties and comparison with other cotton fiber-based sorbents. *Environmental Science & Technology*, *37*(5), 1013–5. Retrieved from http://www.ncbi.nlm.nih.gov/pubmed/12666934

European Communities (Drinking Water) (No. 2) Regulations 2007 (No. S.I. No. 278/2007). (2007). Retrieved from http://www.irishstatutebook.ie/2007/en/si/0278.html

Flach, M. (1997). *Sago palm. Metroxylon sagu Rottb. Promoting the conservation and use of underutilized and neglected crops. 13* (pp. 1–61). Rome, Italy.

Fu, Y., & Chung, D. D. L. (2011). Coagulation of oil in water using sawdust, bentonite and calcium hydroxide to form floating sheets. *Applied Clay Science*, *53*(4), 634–641. doi:10.1016/j.clay.2011.05.014

Garcia-Ubasart, J., Colom, J. F., Vila, C., Hernández, N. G., Blanca Roncero, M., & Vidal, T. (2012). A new procedure for the hydrophobization of cellulose fibre using laccase and a hydrophobic phenolic compound. *Bioresource Technology*, *112*, 341–344. doi:10.1016/j.biortech.2012.02.075

Ghaffari Moghaddam, M., Bin H. Ahmad, F., Basri, M., & Basyaruddin Abdul Rahman, M. (2010). Artificial neural network modeling studies to predict the yield of enzymatic synthesis of betulinic acid ester. *Electronic Journal of Biotechnology*, *13*(3), 1–12. doi:10.2225/vol13-issue3-fulltext-9

Ha, M., Kwon, H., Cheong, H.-K., Lim, S., Yoo, S. J., Kim, E.-J., … Chung, B. C. (2012). Urinary metabolites before and after cleanup and subjective symptoms in volunteer participants in cleanup of the Hebei Spirit oil spill. *The Science of the Total Environment*, *429*, 167–73. doi:10.1016/j.scitotenv.2012.04.036

Ho, Y. S., Ng, J. C. Y., & Mckay, G. (2000). Kinetics of pollutant sorption by biosorbents : review. *Separation and Purification Methods*, *29*(2), 189–232.

Huang, X., & Lim, T. (2006). Performance and mechanism of a hydrophobic – oleophilic kapok filter for oil / water separation. *Desalination 190*, *190*, 295–307. doi:10.1016/j.desal.2005.09.009

Husseien, M., Amer, A. A., & El-maghraby, A. (2008). Experimental investigation of thermal modification influence on sorption qualities of barley straw. *Journal of Applied Sciences Research*, *4*(6), 652–657.

Ibrahim, S., Ang, H., & Wang, S. (2009). Removal of emulsified food and mineral oils from wastewater using surfactant modified barley straw. *Bioresource Technology*, *100*(23), 5744–5749. doi:10.1016/j.biortech.2009.06.070

Ibrahim, S., Wang, S., & Ang, H. M. (2010). Removal of emulsified oil from oily wastewater using agricultural waste barley straw. *Biochemical Engineering Journal*, *49*(1), 78–83. doi:10.1016/j.bej.2009.11.013

Inagaki, M., Kawahara, A., & Konno, H. (2002). Sorption and recovery of heavy oils using carbonized fir fibers and recycling. *Carbon*, *40*(1), 105–111. doi:10.1016/S0008-6223(01)00083-5

Inan, H., Dimoglo, A., Şimşek, H., & Karpuzcu, M. (2004). Olive oil mill wastewater treatment by means of electro-coagulation. *Separation and Purification Technology*, *36*(1), 23–31. doi:10.1016/S1383-5866(03)00148-5

Iritani, E., Katagiri, N., Aoki, K., Shimamoto, M., & Yoo, K.-M. (2007). Determination of permeability characteristics from centrifugal flotation velocity of deformable oil droplets in O/W emulsions. *Separation and Purification Technology*, *58*(2), 247–255. doi:10.1016/j.seppur.2007.03.026

ITOPF. (2011). Oil Tanker Spill Statistics 2011. Retrieved November 13, 2012, from http://www.itopf.com/information-services/publications/documents/STATSPACK2011.pdf

Jebrane, M., & Sèbe, G. (2007). A novel simple route to wood acetylation by transesterification with vinyl acetate. *Holzforschung*, *61*(2), 143–147. doi:10.1515/HF.2007.026

Ji, F., Li, C., Dong, X., Li, Y., & Wang, D. (2009). Separation of oil from oily wastewater by sorption and coalescence technique using ethanol grafted polyacrylonitrile. *Journal of Hazardous Materials*, *164*, 1346–1351. doi:10.1016/j.jhazmat.2008.09.048

Kartikha, C., Vennilamani, N., Pattabhi, S., & Sekar, M. (2010). Utilization of Sago Waste as an Adsorbent for the Removal of Pb (II) from Aqueous Solution : Kinetic and Isotherm Studies. *International Journal of Engineering Science and Technology*, *2*(6), 1867–1879.

Khan, E., Virojnagud, W., & Ratpukdi, T. (2004). Use of biomass sorbents for oil removal from gas station runoff. *Chemosphere*, *57*(7), 681–9. doi:10.1016/j.chemosphere.2004.06.028

Latif Ahmad, A., Ismail, S., & Bhatia, S. (2003). Water recycling from palm oil mill effluent (POME) using membrane technology. *Desalination*, *157*(May), 87–95.

Li, F., Wu, X., Wu, J., Xu, X., & Songjiang, M. (2008). Kinetic Study of Adsorption of Oil from Oilfield Produced Water Using Modified Porous Ceramics Filtration Media in Column Mode. In *The 2nd International Conference on Bioinformatics and Biomedical Engineering* (pp. 2745–2748).

Li, J., & Gu, Y. (2005). Coalescence of oil-in-water emulsions in fibrous and granular beds. *Separation and Purification Technology*, *42*(1), 1–13. doi:10.1016/j.seppur.2004.05.006

Likon, M., Remškar, M., Ducman, V., & Švegl, F. (2013). Populus seed fibers as a natural source for production of oil super absorbents. *Journal of Environmental Management*, *114*, 158–67. doi:10.1016/j.jenvman.2012.03.047

Lim, T., & Huang, X. (2006). In situ oil/water separation using hydrophobic-oleophilic fibrous wall: a lab-scale feasibility study for groundwater cleanup. *Journal of Hazardous Materials*, *137*(2), 820–6. doi:10.1016/j.jhazmat.2006.03.008

Masoumi, H. R. F., Kassim, A., Basri, M., Abdullah, D. K., & Haron, M. J. (2011). Multivariate optimization in the biosynthesis of a triethanolamine (TEA)-based esterquat cationic surfactant using an artificial neural network. *Molecules (Basel, Switzerland)*, *16*(7), 5538–49. doi:10.3390/molecules16075538

Mohamad Daud, W. S. A. B. W., Abdullah, N., Chan, K. Y. M., & Muhammad Azmi, S. (2010). Sago kraft paper: A potential solution to sago industry pollution. In W. D. Yang Li (Ed.), *2010 IEEE International Conference on Advanced Management Science(ICAMS 2010)* (pp. 80–83). Chengdu: IEEE Press. doi:10.1109/ICAMS.2010.5553032

Moriwaki, H., Kitajima, S., Kurashima, M., Hagiwara, A., Haraguchi, K., Shirai, K., … Kiguchi, K. (2009). Utilization of silkworm cocoon waste as a sorbent for the removal of oil from water. *Journal of Hazardous Materials*, *165*(1-3), 266–70. doi:10.1016/j.jhazmat.2008.09.116

Murugananthan, M., Bhaskar Raju, G., & Prabhakar, S. (2004). Separation of pollutants from tannery effluents by electro flotation. *Separation and Purification Technology*, *40*(1), 69–75. doi:10.1016/j.seppur.2004.01.005

Mwaikambo, L. Y., & Ansell, M. P. (2002). Chemical modification of hemp, sisal, jute, and kapok fibers by alkalization. *Journal of Applied Polymer Science*, *84*(12), 2222–2234. doi:10.1002/app.10460

Namasivayam, C., & Sureshkumar, M. V. (2008). Removal of chromium(VI) from water and wastewater using surfactant modified coconut coir pith as a biosorbent. *Bioresource Technology*, *99*(7), 2218–25. doi:10.1016/j.biortech.2007.05.023

Nemec, H. (1994). Fibrillation of cellulosic materials - can previous literature offer a solution? *Lenzinger Berichte*, *74*, 69–72.

New Straits Times Press (Malaysia) Berhad. (2011, October 25). From sago waste to parquet tiles.

Ngarmkam, W., Sirisathitkul, C., & Phalakornkule, C. (2011). Magnetic composite prepared from palm shell-based carbon and application for recovery of residual oil from POME. *Journal of Environmental Management*, *92*(3), 472–9. doi:10.1016/j.jenvman.2010.08.031

Nishi, Y., Iwashita, N., Sawada, Y., & Inagaki, M. (2002). Sorption kinetics of heavy oil into porous carbons. *Water Research*, *36*(20), 5029–36.

Noh, M. F. M., Ngaini, Z., & Wahi, R. (2012). Incorporation of fatty acid derivatives onto sago network for oil absorption. In *ASEAN Sago Symposium 2012: Advances in Sago Research and Development* (p. 34). Kota Samarahan: UNIMAS.

Pasila, A. (2004). A biological oil adsorption filter. *Marine Pollution Bulletin*, *49*(11-12), 1006–12. doi:10.1016/j.marpolbul.2004.07.004

Phalakornkule, C., Mangmeemak, J., & Intrachod, K. (2010). Pretreatment of palm oil mill effluent by electrocoagulation and coagulation. *ScienceAsia*, *36*, 142–149. doi:10.2306/scienceasia1513-1874.2010.36.142

Plazinski, W., Dziuba, J., & Rudzinski, W. (2013). Modeling of sorption kinetics: the pseudo-second order equation and the sorbate intraparticle diffusivity. *Adsorption*, *19*(5), 1055–1064. doi:10.1007/s10450-013-9529-0

Quek, S. Y., Wase, D. A. J., & Forster, C. F. (1998). The use of sago waste for the sorption of lead and copper. *WaterSA*, *24*(3), 251–256.

Radetic, M., Ilic, V., Radojevic, D., Miladinovic, R., Jocic, D., & Jovancic, P. (2008). Efficiency of recycled wool-based nonwoven material for the removal of oils from water. *Chemosphere*, *70*(3), 525–30. doi:10.1016/j.chemosphere.2007.07.005

Rajakovic, V., Aleksic, G., Radetic, M., & Rajakovic, L. (2007). Efficiency of oil removal from real wastewater with different sorbent materials. *Journal of Hazardous Materials*, *143*(1-2), 494–9. doi:10.1016/j.jhazmat.2006.09.060

Rajaković-Ognjanović, V., Aleksić, G., & Rajaković, L. (2008). Governing factors for motor oil removal from water with different sorption materials. *Journal of Hazardous Materials*, *154*(1-3), 558–63. doi:10.1016/j.jhazmat.2007.10.066

Ren, J. L., Sun, R. C., Liu, C. F., Cao, Z. N., & Luo, W. (2007). Acetylation of wheat straw hemicelluloses in ionic liquid using iodine as a catalyst. *Carbohydrate Polymers*, *70*(4), 406–414. doi:10.1016/j.carbpol.2007.04.022

Rengasamy, R. S., Das, D., & Karan, C. P. (2011). Study of oil sorption behavior of filled and structured fiber assemblies made from polypropylene, kapok and milkweed fibers. *Journal of Hazardous Materials*, *186*(1), 526–32. doi:10.1016/j.jhazmat.2010.11.031

Ribeiro, T. H., Rubio, J., & Smith, R. W. (2003). A Dried Hydrophobic Aquaphyte as an Oil Filter for Oil/Water Emulsions. *Spill Science & Technology Bulletin*, *8*(5-6), 483–489. doi:10.1016/S1353-2561(03)00130-0

Said, A. E.-A. A., Ludwick, A. G., & Aglan, H. A. (2009). Usefulness of raw bagasse for oil absorption: a comparison of raw and acylated bagasse and their components. *Bioresource Technology*, *100*(7), 2219–22. doi:10.1016/j.biortech.2008.09.060

Santander, M., Rodrigues, R. T., & Rubio, J. (2011). Modified jet flotation in oil (petroleum) emulsion/water separations. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *375*(1-3), 237–244. doi:10.1016/j.colsurfa.2010.12.027

Sayed, S. A., & Zayed, A. M. (2006). Investigation of the effectiveness of some adsorbent materials in oil spill clean-ups. *Desalination*, *194*(1-3), 90–100. doi:10.1016/j.desal.2005.10.027

Sébastien Lemiere, Carole Cossu-Leguille, Antonio Bispo, Marie-José Jourdain, Marie-Claire Lanhers, Daniel Burnel, P. V. (2005). DNA damage measured by the single-cell gel electrophoresis (Comet) assay in mammals fed with mussels contaminated by the "Erika" oil-spill. *Mutation Research/Genetic Toxicology and Environmental Mutagenesis*, *581*(1-2), 11–21.

Sheintuch, M., & Rebhun, M. (1988). Adsorption isotherms for multisolute systems with known and unknown composition. *Water Research*, *22*(4), 421–430. doi:10.1016/0043-1354(88)90036-X

Shin, C., & Chase, G. G. (2004). Water-in-Oil Coalescence in Micro-Nanofiber Composite Filters. *AIChE Journal*, *50*(2), 343–350.

Singhal, R. S., Kennedy, J. F., Gopalakrishnan, S. M., Kaczmarek, A., Knill, C. J., & Akmar, P. F. (2008). Industrial production, processing, and utilization of sago palm-derived products. *Carbohydrate Polymers*, *72*(1), 1–20. doi:10.1016/j.carbpol.2007.07.043

Sokker, H. H., El-Sawy, N. M., Hassan, M. a, & El-Anadouli, B. E. (2011). Adsorption of crude oil from aqueous solution by hydrogel of chitosan based polyacrylamide prepared by radiation induced graft polymerization. *Journal of Hazardous Materials*, *190*(1-3), 359–65. doi:10.1016/j.jhazmat.2011.03.055

Sokolovic, R., Vulic, T., & Sokolovic, S. (2007). Effect of bed length on steady-state coalescence of oil-in-water emulsion. *Separation and Purification Technology*, *56*(1), 79–84. doi:10.1016/j.seppur.2007.01.028

Srinivasan, A., & Viraraghavan, T. (2008). Removal of oil by walnut shell media. *Bioresource Technology*, *99*(17), 8217–20. doi:10.1016/j.biortech.2008.03.072

Srinivasan, A., & Viraraghavan, T. (2010). Oil removal from water using biomaterials. *Bioresource Technology*, *101*(17), 6594–600. doi:10.1016/j.biortech.2010.03.079

Sun, R., & Sun, X. F. (2002). Structural and thermal characterization of acetylated rice, wheat, rye, and barley straws and poplar wood fibre. *Industrial Crops and Products*, *16*(3), 225–235. doi:10.1016/S0926-6690(02)00050-X

Sun, X. (2004). Acetylation of sugarcane bagasse using NBS as a catalyst under mild reaction conditions for the production of oil sorption-active materials. *Bioresource Technology*, *95*(3), 343–350. doi:10.1016/j.biortech.2004.02.025

Suni, S., Kosunen, A., Hautala, M., Pasila, A., & Romantschuk, M. (2004). Use of a by-product of peat excavation, cotton grass fibre, as a sorbent for oil-spills. *Marine Pollution Bulletin*, *49*(11-12), 916–21. doi:10.1016/j.marpolbul.2004.06.015

Tansel, B., & Pascual, B. (2011). Removal of emulsified fuel oils from brackish and pond water by dissolved air flotation with and without polyelectrolyte use: pilot-scale investigation for estuarine and near shore applications. *Chemosphere*, *85*(7), 1182–6. doi:10.1016/j.chemosphere.2011.07.006

Tansel, B., & Sevimoglu, O. (2006). Coalescence and Size Distribution Characteristics of Oil Droplets Attached on Flocs After Coagulation. *Water, Air, and Soil Pollution*, *169*(1-4), 293–302. doi:10.1007/s11270-006-3110-3

Tansel, B., & Vilar, F. (2005). Enhancement of media filter performance with coagulant use for treatment of diesel oil contaminated surface water. *Desalination*, *173*(1), 69–76. doi:10.1016/j.desal.2004.08.028

Teas, C., Kalligeros, S., Zanikos, F., Stoumas, S., Lois, E., & Anastopoulos, G. (2001). Investigation of the effectiveness of absorbent materials in oil spills clean up. *Desalination*, *140*, 259–264. doi:10.1016/S0011-9164(01)00375-7

Teli, M. D., & Valia, S. P. (2013). Acetylation of banana fibre to improve oil absorbency. *Carbohydrate Polymers*, *92*(1), 328–333. doi:10.1016/j.carbpol.2012.09.019

Tsibranska, I., & Hristova, E. (2011). Comparison of different kinetic models for adsorption of heavy metals onto activated carbon from apricot stones, *43*(3), 370–377.

USDA. (2012). World vegetable oil consumption 2011. *Soy Stats*. Retrieved from http://www.soystats.com/2012/page_35.htm

US-EPA. (2011). Sorbents. *Emergency Management*. Retrieved May 07, 2012, from http://www.epa.gov/oem/content/learning/sorbents.htm

Vikineswary, S., Shim, Y. L., Thambirajah, J. J., & Blakebrough, N. (1994). Possible microbial utilization of sago processing wastes. *Resources, Conservation and Recycling*, *11*(1-4), 289–296. doi:10.1016/0921-3449(94)90096-5.

Wang, J., Zheng, Y., & Wang, A. (2012). Effect of kapok fiber treated with various solvents on oil absorbency. *Industrial Crops and Products*, *40*, 178–184. doi:10.1016/j.indcrop.2012.03.002

Weber, W. J. J., McGinley, P. M., & Katz, L. E. (1991). Sorption phenomena in subsurface systems: concepts, models and effects on contaminat fate and transport. *Water Research, 25*(5), 499–528. doi:10.1016/0043-1354(91)90125-A

World Health Organization. (2011). *Guidelines for drinking-water quality, fourth edition 2011*. Retrieved from http://www.who.int/water_sanitation_health/publications/2011/dwq_chapters/en/index.html

Wu, T. Y., Mohammad, a. W., Md. Jahim, J., & Anuar, N. (2007). Palm oil mill effluent (POME) treatment and bioresources recovery using ultrafiltration membrane: Effect of pressure on membrane fouling. *Biochemical Engineering Journal*, *35*(3), 309–317. doi:10.1016/j.bej.2007.01.029

Wu, T. Y., Mohammad, A. W., Jahim, J. M., & Anuar, N. (2010). Pollution control technologies for the treatment of palm oil mill effluent (POME) through end-ofpipe processes. *Journal of Environmental Management*, *91*(7), 1467–90. doi:10.1016/j.jenvman.2010.02.008

Xiao-bing, L. I., Jiong-tian, L. I. U., Yong-tian, W., Cun-ying, W., & Xiao-hua, Z. (2007). Separation of oil from wastewater by column flotation. *Journal of China University of Mining & Technology*, *17*(4), 546–551.

Yang, C. (2007). Electrochemical coagulation for oily water demulsification. *Separation and Purification Technology*, *54*(3), 388–395. doi:10.1016/j.seppur.2006.10.019

Yi, X. S., Yu, S. L., Shi, W. X., Sun, N., Jin, L. M., Wang, S., … Sun, L. P. (2011). The influence of important factors on ultrafiltration of oil/water emulsion using PVDF membrane modified by nano-sized TiO2/Al2O3. *Desalination*, *281*, 179–184. doi:10.1016/j.desal.2011.07.056

Zhang, W., Okubayashi, S., & Bechtold, T. (2005). Fibrillation tendency of cellulosic fibers -part 3. Effects of alkali pretreatment of lyocell fiber. *Carbohydrate Polymers*, *59*(2), 173–179. doi:10.1016/j.carbpol.2004.09.007

Zhou, Y.-B., Tang, X.-Y., Hu, X.-M., Fritschi, S., & Lu, J. (2008). Emulsified oily wastewater treatment using a hybrid-modified resin and activated carbon system. *Separation and Purification Technology*, *63*(2), 400–406. doi:10.1016/j.seppur.2008.06.002