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Pemanfaatan Limbah Cangkang Kelapa Sawit dalam Pengolahan *Palm Oil Mill Effluent* dengan Metode *Pretreatment* Sodium Hidroksida

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Abstract

POME, an oily wastewater generated by palm oil processing mills which 1 ton of palm oil fruit bunch produces 100-450 kg of POME (from sterilization, clarification, and hydrocyclone discharges). POME contains 0.6-0.7% oil and grease which has to be treated firstly before discharged. Experiments consist of two stages which are pretreatment and adsorption process. They were carried out to find out effect of pretreatment solution concentration and adsorbent dosage toward percentage of yield. From 1 ton of palm oil fruit bunch as much as 65 kg palm kernel shells are usually produced which can be used to adsorb oil in POME. Pretreatment process was done by soaked the adsorbent using 1, 1.5, and 2.5 M sodium hydroxide solutions. In the adsorption process, 100 ml oil solution with concentration of 6000 ppm was added whereas the dosages of adsorbent varied as follow 2, 3, and 4 gram and was done in batch, room temperature, -10+20 mesh, 40 minutes contact time, and 200 rpm stirring rate with analysis including: the yield of oil adsorbed on adsorbent (percentage of yield) and moisture content. The result showed that pretreatment using sodium hydroxide solution has decreased the oil content in POME up to 73.9% (w/w).

Keywords: *Oil adsorption, Waste management, Palm kernel shell, POME, Residue oil*

Introduction

Palm oil industry is a main economic contributor in Indonesia. Palm oil mill effluent (POME) is the largest waste contributor in the palm oil mills which 1 ton of palm oil fruit bunch produces 350-450 kg of POME (from sterilization and clarification) and 100-150 kg of POME (from hydrocyclone discharges) (Ria Purnama et al., 2012). POME is a colloidal suspension that contains 95-96% of water, 0.6-0.7% of oil and grease, and 4-5% of total solids including 2-4% suspended solids originated from the mixture of sterilized condensat, separator sludge, and hydrocyclone wastewater (Ahmad et al., 2005). It is a thick brownish color liquid and discharged at a temperature between 80 and 90ºC. The pH ranging of POME is 4.0 to 5.0. Table 1 shows the characteristics of raw POME.

Table 1. Characteristics of POME (Ahmad et al., 2005)

Parameter	Concentration (mg/l)
Oil and grease	4,000-6,000
Biochemical oxygen demand	25,000
Chemical oxygen demand	50,000
Total solid	40,500
Suspended solids	18,000
Total volatile solids	34,000
Ammonicals nitrogen	35
Total nitrogen	750

One of the major problems with POME is its residual oil content. POME contains about 4000-6000 mg/l oil and grease (Ahmad, Sumathi, and Hameed, 2005). POME distributes a high concentration of surface active compounds like phospholipids (10 wt%) and glycolipids (6 wt%). The residueoil has to be removed from wastewater to avoid problems in the subsequent water treatment units and biological treatment stages. When it is discharged into waterways, it can contaminate drinking water for human and animal communities. It can be particularly harmful to aquatic communities by creating highly acidic environments or causing eutrophication (where excessive alga growth occurs on the surface of the water). POME also typically released into open air holding ponds for remediation, thereby releasing carbon dioxide, methane, and hydrogen sulphide, all of which contribute to global climate change.

The maximum allowable limit set by regulation of environment minister Indonesia for oil and grease level is 25 mg/l (Kemen, 2014). Hence, the challenge of balancing the POME into more environmental friendly waste requires a sound and efficient treatment and disposal approach.Numerous techniques to remove residual oil from POME, such as chemical-biological (Rivas et al., 2001), solvent extraction method (Ahmad et al., 2003), sedimentation, flocculation and coagulation (Ahmad et al., 2003; Qiu et al., 1995; Kamal et al., 2000) methods have been reported. The removal of residual oil by adsorption using palm kernel shells as the adsorbent is very promising and requires further study. Compositionally, palm kernel shells are high in lignin and hemicellulose which make palm kernel shells have the ability to adsorb the residue oil in POME. Many researches have been conducted on removal of residual oil using palm kernel shells with prior conversion into activated carbon but they require high temperature (Rugayah et al., 2017). In the present study, a series of adsorption experiments were conducted to evaluate the possibility of the use of palm kernel shells as adsorbent for residue oil removal from POME without convert it into activated carbon.

Adsorbent has been developed for a wide range of separations. Commercial materials are usually used in the form of pellets, granules or beads, although powder is occasionally used. Since adsorption is a surface-related phenomenon, the useful adsorbents are all characterized by a large surface area per unit of weight. The study of adsorption for the treatment of wastewater has been proven to be less expensive, effective for wastewater treatment depending on the type of adsorbent used (Ahmad et al., 2005). Palm kernel shells, as the adsorbent, are solid waste generated from palm oil mill. Palm kernel shells are the shell fractions left after the nut has been removed in the palm oil mill. From 1 ton of palm oil fruit bunch as much as 65 kg palm kernel shells are usually produced (Haryanti et al., 2014). In the palm oil value chain, the utilization rate of palm kernel shells are comparatively very low. Palm kernel shells is commonly used in combustion processes, especially at oil mills as boiler fuel to generate heat and electricity although palm kernel shells itself is not well regarded as a fuel due in part to smoke emissions.

Palm kernel shells will be pretreated first to increase its porosity by using sodium hydroxide. The aim of this paper was to prove the adsorption of residue oil from POME by palm kernel shells. Adsorptions were carried out through a series of batch adsorptions.

Materials and Methods

Experimental Materials

Samples of POME used in this study were made from *minyak goreng Bimoli* with concentration of 6000 ppm. Palm kernel shells were obtained from PT. Surya Utama Nabati, Indonesia. Prior the process, the shells were cleaned and dried under the sun for about 24 hours and turned occasionally to remove moisture.

Pretreatment Experiments

Palm kernel shells were pretreated with 1, 1.5, and 2.5 M sodium hydroxide solutions in sealed beaker glass for 24 hours at room temperature. The pretreated palm kernel shells were washed with aquadest which was sufficient to neutralize the pH of the substrate. The wet solids were dried in an oven 60ºC for 24 hours. Furthermore, the palm kernel shells were sieved using -10+20 mesh and dried in an oven again 60ºC before being used as an adsorbent.

Adsorption Experiments

The batch adsorption experiments performed in 250 ml beaker glass containing 100 ml sample of POME and 2 g of the adsorbent was added. The beaker glass put in a mixer agitator under constant stirring rate (200 rpm) for 40 min. The type of agitator used is pitch blade turbine generator in order to be able to blend oil, water, and palm kernel shells which have different density one to another. Furthermore, the adsorbent was filtered using what man filter paper. The residue adsorbent was dried in an oven at 60ºC and weighed. The same procedure was repeated for 3 g and 4 g of the adsorbent, respectively. The yield of oil adsorbed on adsorbent (percentage of yield) was calculated using equation (1).

$$\%yield = [(m_1 - m_0)/m_0] \times 100\% \qquad (1)$$

Where m_1 and m_0 are respectively the final and initial mass of adsorbent (g). Water content in the adsorbent was measured using moisture analyzer.

Results and Discussion

Effect of Concentration of Pretreatment Solution

Pretreatment process was carried out to using sodium hydroxide break the bonding among cellulose, hemicelluloses, and lignin. Ion OH^- from sodium hydroxide reacts with lignin to break the bond and basic structure of lignin which are alkyl-aryl, aryl-aryl, and alkyl-alkyl ether bonds. Those compounds react with Na^+ to produce polar salt and dissolved with water. Termination of lignin bonds are indicated by the presence of black in the residue sodium hydroxide solution and also cause the formation of pores in the adsorbent (Suyati, 2008). The formation of

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pores increases the surface area of palm kernel shells so adsorption capacity of palm kernel shells also increase (Erlina et al., 2015). Upon the completion of pretreatment process, palm kernel shells were neutralized with aquadest water until pH 7.0 in order to remove the residual of ion OH^- in the shells. The presence of ion OH^- could replace oil solution bound with cellulose (Handayani, 2010). The effect of the variation of pretreatment solution from 1 to 2.5 M used with the same initial oil concentration (6000 mg/l) was shown in Figure 1. Increasing sodium hydroxide concentration from 1 M to 1.5 M significantly increases total lignin removal which can be seen by the increased percentage of yields. In fact, the increasing of sodium hydroxide concentration from 1.5 M to 2.5 M decreases percentage of yields. The higher concentration of pretreatment solution used, the more bonding was broken which shows the increase of pores formed on the surface of the adsorbent (Johari et al., 2016). The larger pores are formed, the greater possibility the oil which has been bounded releases to the solution. In the other hand, structure of lignocelluloses was shown in Figure 2. Lignin has a rigid and impermeable resistance so the oil can’t be adsorbed into the adsorbent. Hence, cellulose and hemicellulose are preferable to bind oil molecules. Cellulose has a long chain which is linked together by hydrogen and van der walls bonds while hemicellulose has branches with shorter chain than cellulose thus its branches make oil molecules are easier bounded (Bajpai, 2016). The highest percentage of yield is in 1.5 M of sodium hydroxide solution.

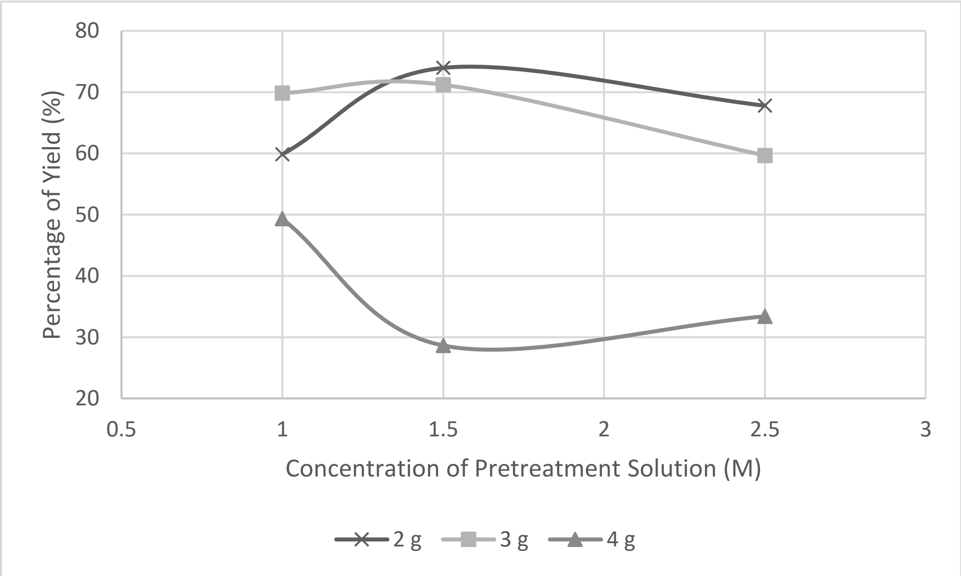

Figure 1. Percentage of yield vs. concentration of pretreatment solution

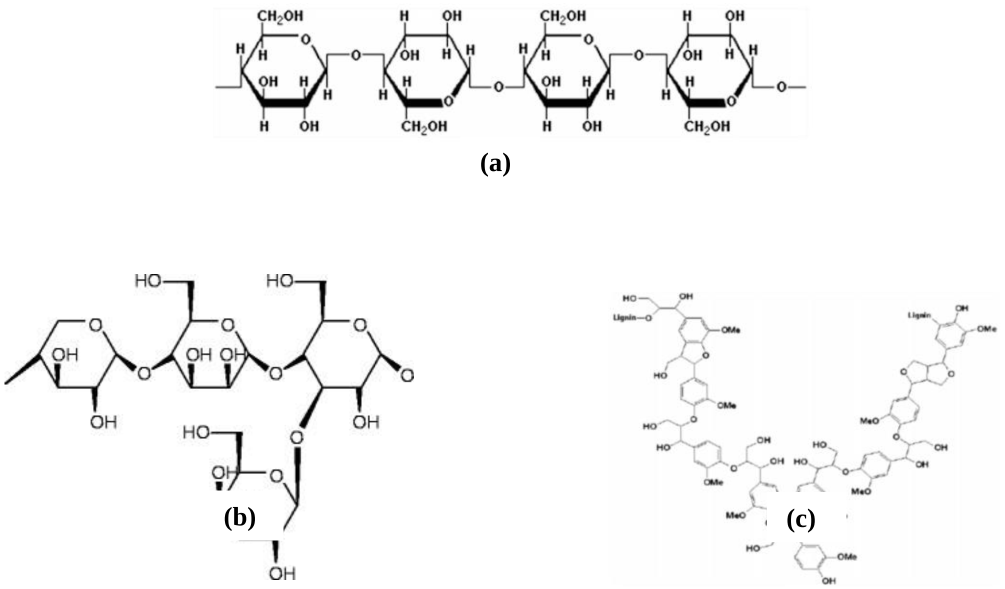

Figure 2. Structure of lignocelluloses (a) cellulose (b) hemicellulose (c) lignin (Bajpai, 2016)

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Effect of Adsorbent Dosage

Samples of POME were treated with 3 different weight dosages of palm kernel shells which are 2, 3, and 4 g. The initial concentration of oil in POME was 6000 mg/l. Figure 1 shows the effect of palm kernel shells dosage towards the percentage of yield of oil adsorbed on adsorbent. It was noticed that when the weight dosage of palm kernel shell increased, the percentage of yield decreased. The amount of palm kernel shell needed to achieve about 74% yield of oil adsorbed on adsorbent from POME at 200 rpm for 40 min of contact was 2 g. Palm kernel shells could almost adsorb 75% the residue oil in the POME at lower dosage. Increasing adsorbent dosage significantly decrease percentage of yield due to the palm kernel shells are hygroscopic so after the palm kernel shells were put into an oil solution, it formed lumps between one granule of adsorbent with the other granules. These lumps caused overall surface area of the adsorbent decreased (Pandia and Budi, 2016). Palm kernel shells have lignin and hemicellulose which attract oil to bind thus the residue oil to bind with palm kernel shells. Residue oil adsorption was promising with palm kernel shells, without any noticeable advantage at higher dosage levels and excellent performance at lower dosage.

Conclusions

As a conclusion to this finding, the destabilization of oil in water was successfully performed by the application of palm kernel shells, which shows synergistic enhancement for the effective adsorption of residue oil from palm oil mill effluent (POME). Increasing concentration of pretreatment could increase percentage of yield while percentage of yield decreased when the weight dosage of palm kernel shells increased. Sodium hydroxide solution can remove oil content in POME up to 73.9% (w/w) with the optimum of adsorbent dosage is 2 g. Palm kernel shells which is derived from palm oil industry waste products would be very useful as a residue oil adsorbent in any oily wastewater treatment.

References

ABD Wafti NS, Nang Lau HL, Loh SK, Aziz AA, Zulkifli Rahman AB, May CY. Activated carbon from oil palm biomass as potential adsorbent for palm oil mill effluent treatment. Journal of Oil Palm Research 2017; 29 (2): 278-290.

Ahmad AL, Bhatia S, Ibrahim N, Sumathi S. Adsorption of residual oil from palm oil mill effluent using rubber powder. Brazilian Journal of Chemical Engineering 2005; 22 (3): 371-379.

Ahmad AL, Sithamparam K, Ismail S. Extraction of residual oil from palm oil mill effluent (POME) using organic solvent. AJSTD 2003; 20: 385.

Ahmad AL, Sumathi S, Hameed BH. Adsorption of residue oil from palm oil mill effluent using powder and flake chitosan: Equilibrium and kinetic studies. Water Research 2005; 39: 2483-2494.

Bajpai P. Pretreatment of lignocellulosic biomass for biofuel production. Springer Singapore: Singapore. 2016: 7-12.

Edmund Okoroigwe C, Christopher Saffron M, Pascal Kamdem D. Characterization of palm kernel shell for materials reinforcement and water treatment. J. Chem. Eng. Mater. Sci. 2014; 5 (1): 1-6.

Erlina, Umiatin, Budi E. Pengaruh konsentrasi larutan KOH pada karbon aktif tempurung kelapa untuk adsorpsi logam Cu. SNF 2015; IV (VII): 55-60.

Handayani AW. Penggunaan selulosa daun nanas sebagai adsorben logam berat CD (II). University of Sebelas Maret, minithesis, 2010.

Haryanti A, Norsamsi, Fanny Sholiha PS, Pralisa Putri N. Studi pemanfaatan limbah padat kelapa sawit. Konversi 2014; 3 (2): 20-29.

Heraldy E, Osa RR, Suryanti V. Adsorption of procion red MX 8B using spent tea leaves as adsorbent. AIP Conf. Proc. 2016; 1710 (030025): 1-9.

Johari K, Saman N, Song ST, Chin CS, Kong H, Mat H. Adsorption enhancement of elemental mercury by various surface modified coconut husk as eco-friendly low-cost adsorbents. International Biodeterioration & Biodegradation 2016; 109: 45-52.

Kamal A, Mohammed OJ, Azzam NIA. Olive mills effluent (OME) wastewater posttreatment using activated clay. Sep. Purification Techno 2000; 20:225.

Kemen LH. Baku mutu air limbah. Peraturan Menteri Lingkungan Hidup Republik Indonesia Nomor 5, 2014.

Pandia S, Budi W. Pemanfaatan kulit jengkol sebagai adsorben dalam penyerapan logam Cd (II) pada limbah cair industri pelapisan logam. Jurnal Teknik Kimia USU 2016; 5 (4): 57-63.

Qiu Z, Zhang Y, Fang Y. Removal of oil from concentrated wastewater by attapulgite and coagulan. Water Quality Res. J. Canada 1995; 30: 89.

Ria Purnama R, Chumaidi A, Saleh A. Pemanfaatan limbah cair CPO sebagai perekat pada pembuatan briket dari arang tandan kosong kelapa sawit. Jurnal Teknik Kimia 2012; 18 (3): 43-53.

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Rivas FJ, Beltran FJ, Gimeno O, Alvarez P. Chemical-biological treatment of table olive manufacturing wastewater. J. Environmental Eng 2001; 127: 611.

Rugayah AF, Astimar AA, Norzita N. Preparation and characterisation of activated carbon from palm kernel shell by physical activation with steam. Journal of Oil Palm Research 2014; 26 (3): 251-264.

Suyati. Pembuatan selulosa asetat dari limbah serbuk gergaji kayu dan identifikasinya. Bandung Institute of Technology, Magister thesis, 2008.

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Lembar Tanya Jawab

Moderator : Erlinda Ningsih (Teknik Kimia ITATS Surabaya)
Notulen : Briana Bellis Linardy (UPN "Veteran" Yogyakarta)

1. Penanya : Erlinda Ningsih(Teknik Kimia, ITATS)
   Pertanyaan :
   - Apakah uji SEM luas permukaan dilakukan?
   - Apa dasar pemilihan suhu?

   Jawaban :
   - Sedang menunggu hasil dari uji sebelum dan sesudah absorbsi.
   - Dipilih 60^{o}C berdasarkan premis yang didapat, dan apabila suhu terlalu tinggi dapat menjadi karbon aktif.

2. Penanya : Dewi Purnama Sari (UGM)
   Pertanyaan : Mengapa batasan penelitian hanya sampai cangkang, padahal jika sampai karbon aktif dapat menjadi absorber yang lebih baik?
   Jawaban : Karena memerlukan suhu tinggi untuk menjadi karbon aktif, dan biaya lebih mahal. Maka dipilih cangkang yang lebih murah