Removal of Residual Oil from Palm Oil Refinery Factory Effluent by Chitosan and Its Derivatives

A. HASSAN¹, M.P. ABDULLAH^{1,2,*} and W.M.A.W.M. KHALIK^{2,3,*}

¹School of Chemical Sciences and Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Malaysia

²Centre for Water Research and Analysis, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Malaysia

³School of Marine and Environmental Sciences, Universiti Malaysia Terengganu, 21030 Kuala Nerus, Malaysia

*Corresponding authors: Tel: +60 8 9214268, email: mpauzi@ukm.edu.my, wan.afiq@umt.edu.my

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Chitosan and its derivatives namely oleoyl chitosan, oleoyl methylene phosphonic chitosan and methylene phosphonic chitosan as potential sorbents to clean up the residual oil were successfully evaluated. Batch experiment technique was employed to identify the best sorbent. The main factors affecting the sorption namely the initial concentration of residual oil, weight of sorbent dosage, contact time and sample pH were tested. The optimum sorption capacity of oleoyl chitosan and chitosan were 128.65 and 120.68 mg/g, respectively at sorbent dosage (0.1 mg), the initial concentration of residual oil (1g/L), contact time (30 min) and pH effluent (pH 4). Meanwhile, the optimum sorption capacity for oleoyl methylene phosphonic chitosan and methylene phosphonic chitosan were 118.91 and 77.57 mg/g, respectively at sorbent dosage (0.1 mg) with the initial concentration of residual oil of (1 g/L) but less contact time (15 min) and effluent (pH > 6). This study revealed oleoyl chitosan type was the best sorbent compared to chitosan, oleoyl methylene phosphonic chitosan and methylene phosphonic chitosan. It is most suitable as sorbent not only because it has the highest sorption capacity, but also exhibits the non-toxic chitosan derivative.

Keywords: Chitosan, Residual oil, Palm oil refinery effluent.

INTRODUCTION

The Malaysian palm oil industry is growing rapidly and becoming a significant agriculture-based industry in this country. Table-1 shows the increment of total productions of crude palm oil (CPO) in Malaysia between 2015 and 2016 [1]. Crude palm oil is produced from the mesocarp and kernel of palm fruit in a process commonly performed in the palm oil mill. Later, crude palm oil will be refined to produce refined bleached deodorized palm oil (RBDPO) and palm fatty acid distillates (PFAD) through physical refining method or neutralized bleached deodorized palm oil (NBDPO) if the refining process uses the chemical refinery method. Physical refinery method is a preferable method due to the lower cost and fewer steps of refinery [2]. In general, refining process involves four main steps, namely degumming, bleaching, deodorization, and alkali neutralization (only in a chemical refinery). Bleaching and deodorizing steps are the steps where most of the effluent water is produced.

The physico-chemical properties of palm oil refinery factory effluent (PORFE) (Table-2) have different amounts from the palm oil mill effluent (POME) but still contain residual oil which should be treated before legally allowed to be discharged into any receiving waterway [3]. In Malaysia,

TABLE-1
MALAYSIAN PRODUCTION OF
CRUDE PALM OIL IN 2015 AND 2016

Crude palm oil production	2015	2016
Johor	3117619	2745389
Kedah	315649	222309
Kelantan	281412	278086
Negeri Sembilan	680285	542561
Pahang	2950300	2422681
Perak	1989285	1629338
Selangor	503878	418090
Terengganu	496529	445965
Other States	201510	182219
Peninsular Malaysia	10536467	8886638
Sabah	5722967	4847253
Sarawak	3702147	3585286
Sabah/Sarawak	9425114	8432539
Total production in Malaysia (tonnes)	19961581	17319177

the standard permissible limits for discharged effluent water currently enforced by the Department of Environment Malaysia are summarized in Table-2.

The concentration of residual oil produced in PORFE is far exceeding the limit as required by the effluent standard. To overcome this issue, a biological treatment through degradation

TABLE-2
PHYSICO-CHEMICAL CHARACTERISTIC OF POME, PORFE AND STANDARD LIMIT

Characteristic	POME	PORFE	Standard limit
Colour	Brownish	Yellowish	Not available
pH	4-5	4-5	5-9
Oil and grease (mg/L)	4000-6000	1480-2000	50
Biochemical oxygen demand (mg/L)	25000	2600	100
Chemical oxygen demand (mg/L)	50000	3000	Not available
Total solids (mg/L)	40500	152	Not available
Ammonical nitrogen (mg/L)	35	0.5	150

by the microorganism is normally employed either by using the aerobic or anaerobic process. However, there are drawbacks due to it being time consuming and non-reusable of residual oil for other purposes [4].

The sorption of residual oil such as coagulants, namely aluminum chloride, ferrous sulfate, aluminum sulfate, ferric chloride and hydrated lime is widely used in the conventional treatment systems. This sorbent is effective, low-cost, easy to handle and easily available. Aluminum sulfate (alum) and poly-aluminum chloride are the most popular coagulants applied in the treatment systems. However, the usage of these coagulants leads to the presence of hazardous activated sludge containing residual aluminum which may cause environmental toxicity. It has been pointed out that the intake of a large amount of aluminum salt may cause Alzheimer's disease [5].

Chitosan is a natural sorbent which is a non-toxic material and cationic biodegradable biopolymer. It can be produced by the extensive deacetylation of chitin obtained from shrimp shells. The structure of pure chitosan chain has positively charged functional group amine (NH_3^+) which is responsible for the poly-electrolyte behaviour. The drawback of pure chitosan is that it is only effective in acidic medium condition [6]. To enhance the ability of chitosan as oil residual sorbents, a modification of pure chitosan chain is necessary [7]. The aim of this study is to prepare derivatives of chitosan *via* acylation reaction to make it suitable for the sorption of the residual oil. The non-toxicity of modified chitosan is perhaps not only suitable for good sorbent but also can be reused as additive or fertilizer in agriculture sector such as vermi-composting [8].

EXPERIMENTAL

Palm oil refinery factory effluent (PORFE) samples were collected from Ngo Chew Hong (M) Oils and Fats Company located at Semenyih, Malaysia. The pure chitosan was supplied by a local manufacturer, Chitochem (M) Sdn Bhd. Other chemicals namely acetic acid, sodium hydroxide pellets, oleoyl chloride, and *n*-hexane with analytical grade were purchased from Merck (Darmstadt, Germany).

Synthesis of oleoyl chitosan: Approximately 5 g pure chitosan was dissolved in 1 % acetic acid solution. Then pH was adjusted to 6.3 with 0.1 M NaOH solution. Oleoyl chloride (5 mL) dissolved in 50 mL chloroform was added into the chitosan solution. The mixture solution was stirred for 6 h after that the pH solution was once again adjusted to pH 6.9 with 0.1 M NaOH solution. A polar solvent called acetone was used to precipitate the chitosan derivative. Oleoyl chitosan was filtered and washed with methanol and then dried for 2 days [9].

Synthesis of N-methylene phosphonic chitosan: About 5 g pure chitosan was dissolved into 250 mL of 1 % acetic acid solution. The temperature was increased to 50°C before phosphorus acid was added to the solution. The temperature was then increased again to 70 °C and 5 mL of 35 % formaldehyde was added to the solution. The mixture solution was refluxed for 8 h. Acetone was then added to the solution to precipitate the derivative. The precipitated derivative was washed with acetone in Soxhlet to remove the excess phosphorus acid. Finally, N-methylene phosphonic chitosan was filtered and dried for 2 days.

Synthesis of oleoyl N-methylene phosphonic chitosan: Oleoyl methylene phosphonic chitosan was prepared by dissolving 5 g of N-methylene phosphonic chitosan in a mixture of methanol and water (80:20) before it was stirred for 24 h. The pH of mixture solution was adjusted to pH 6.3. Oleoyl chloride, previously dissolved in 50 mL of chloroform, was added and continuously stirred for 6 h. After that the pH of mixture was adjusted again to pH 6.9 with 0.1 M NaOH solution. Acetone was then used to precipitate the derivative. Oleoyl methylene phosphonic chitosan was then filtered and washed with methanol and dried for 2 days.

Characterization of chitosan and its derivatives: The presence of functional groups in chitosan backbone was determined using ATR-FTIR (Spectrum Model BX, Perkin Elmer). Meanwhile, the elemental analysis was performed by using Elemental Analyzer (Model EA 1108, Fisons Instruments) to determine C, H, and N of chitosan and its derivatives. The morphology of surface sorbents was analyzed using the scanning electron microscopy.

Extraction and analysis of residual oil: The residual oil from PORFE was extracted using liquid-liquid extraction. The original sample of PORFE was transferred into 1 L of a separating funnel. *n*-Hexane (30 mL) was added to the separating funnel as a solvent extraction. The samples were shaken vigorously for 2 min and left for 5 min to allow separation. The extraction process was repeated twice with two more portions of 30 mL of *n*-hexane. Then, the upper solvent layer was drained through a funnel containing a piece of filter paper and 2 g of anhydrous sodium sulfate into 100 mL beaker. The residual oil was then concentrated using rotavapor. The extracted oil was transferred into a 10 mL vial before being placed into a desiccator for further drying of any traces of solvent. The final measurement was performed to get the constant weight.

The concentration of residual oil was measured before and after the batch experiment using UV-Vis spectrometry (Model UV-2450, Shimadzu) at 260 nm absorption wavelength. The standard solution was prepared by dissolving 1 g of residual

oil extracted from PORFE. A series of dilution concentration was prepared at six level of concentrations (100, 200, 300, 400, 500 and 700 mg/L). The calibration curve was obtained by plotting the adsorption *versus* concentration of the residual oil.

Sorption procedure: The batch shaker tests were conducted for the sorption of residual oil by chitosan and its derivatives. A mixture of water was prepared by mixing methanol samples (100 mL) with extracted residual oil in a 250 mL conical flask followed by an addition of sorbent. The conical flasks were placed into the orbital shaker for sorption processes depending upon different mixing time (5-60 min). The next batch experiments involved a series of sorbent dosage (0.1 -1.0 mg), pH sample (4-10), and initial concentration of residual oil (20, 25, 50, 75 and 100%). The sorption capacity was calculated [10] using the formula given as follows:

$$\text{Sorption capacity } (q_e) = \frac{(C_i - C_f)}{1000w} \quad (1)$$

where q_e = sorption capacity (mg/g), C_i = initial concentration (mg/L), C_f = final concentration (mg/L), w = amount of sorbent (g) while V = volume of sample.

RESULTS AND DISCUSSION

Chitosan and its derivatives were characterized using the Fourier transform infrared spectroscopy as illustrated in Fig. 1. The functional groups of N-H and O-H were present in chitosan and its derivatives were shown at peaks 3368-3361 cm^{-1} . The carbonyl group due to NH-COCH_3 (C=O bond) group appeared in chitosan at 1638 cm^{-1} meanwhile for N-methylene phosphonic chitosan, oleoyl methylene phosphonic chitosan and oleoyl chitosan at 1630, 1637 and 1638 cm^{-1} , respectively. The C-O stretching peak for pure chitosan was observed at 1149

cm^{-1} , meanwhile for N-methylene phosphonic chitosan, oleoyl methylene phosphonic chitosan, and oleoyl chitosan appeared at 1147, 1149 and 1154 cm^{-1} , respectively [9].

The FTIR spectrum also showed two peaks (C-H stretching 2925-2853 cm^{-1}) for oleoyl chitosan compared to only one peak 2884 cm^{-1} for pure chitosan [11]. The presence of peak at 1534 cm^{-1} for oleoyl chitosan and N-methylene phosphonic chitosan showed the N-H bending for secondary amine in chitosan structure. A new peak appeared at 1421 cm^{-1} due to P-CH₂ bonding, (1056 and 1025 cm^{-1}) of P-OH shifting and at 2387 cm^{-1} (P-H bonding) showed three characteristics of phosphonic group [12].

Two peaks (2925-2853 cm^{-1}) were obtained for oleoyl methylene phosphonic chitosan compared to only one peak (2884 cm^{-1}) for N-methylene phosphonic chitosan, corresponding to the stretching of C-H [13]. Both derivatives also presented three phosphonic group characteristic bands at which one peak appeared at 2325 cm^{-1} (split) due to P-H stretching, shifting at 1065 and 1025 cm^{-1} corresponding to P-OH, and one peak at 1421 cm^{-1} due to P-CH₂ bonding. The presence of one peak at 1534 cm^{-1} showed the N-H bending for secondary amine.

The amount of C, H, and N elements in chitosan, chitosan derivatives and their degrees of substitution are shown in Table-3.

The morphology surface of all sorbents was analyzed and illustrated in Figs. 2 and 3, respectively. An average of particle size was found to be 552.78 nm (pure chitosan), 273.86 nm (N-methylene phosphonic chitosan), 301.88 nm (oleoyl methylene phosphonic chitosan) and 539.74 nm (oleoyl chitosan), respectively.

Fig. 1. ATR-FTIR spectrum a) chitosan b) N-methylene phosphonic chitosan c) oleoyl methylene phosphonic chitosan and d) oleoyl chitosan

Fig. 2. Morphology surface of sorbent a) pure chitosan and b) oleoyl chitosan

Effect of sorbent dosage: An addition of increased sorbent dosage would increase the sorption capacity until it reached a saturation point (Fig. 4). In fact, the saturation levels were reached when there was no more active site compared to the amount of oil in effluent samples.

Effect of pH: The sorption capacity of pure chitosan is higher in acidic condition. The presence of amino group in chitosan chain would attract the carbonyl group of residue oil

TABLE-3
ELEMENTAL ANALYSIS OF C, H, N AND S

Derivatives	Molar ratio N	Molar ratio C	C/N	Degree of substitution
Chitosan	0.547	3.279	5.994	–
Oleoyl chitosan	0.231	2.854	12.312	0.351
N-Methylene phosphoric chitosan	0.302	2.029	6.709	0.358
Oleoyl methylene phosphonic chitosan	0.246	1.771	7.173	0.059

Fig. 3. Morphology surface of sorbent a) N-methylene phosphonic chitosan and b) oleoyl methylene phosphonic chitosan

Fig. 4. Sorption capacity of sorbent against sorbent dosage

and lead to electrostatic attractions between the residual oil molecules and adsorption site of chitosan [6]. The low pH will protonate more amino groups in chitosan to form ammonium ion [14]. Therefore, an electrostatic attraction between negatively charged carbonyl group of residual oil and positively charged adsorption sites of chitosan will be increased. The presence of oleoyl group in chitosan backbone will provide a more hydrophobic surface area, which can interact with non-polar group of residual oil in acidic and neutral conditions [15] and in the meantime, there are still amino groups that can attract carbonyl group of residual oil in acidic condition [5]. A similar phenomenon was observed for oleoyl methylene phosphonic chitosan.

In case of methylene phosphonic chitosan, the recovery process after the sorption of residual oil is difficult since methylene phosphonic chitosan dissolve more in acidic condition. The cationic properties of chitosan also decrease with the presence of PO_3^{2-} which could not further interact with the carbonyl ions of residual oil. The sorption process of residual oil seems to increase for pH 9 and 10 for all the sorbents. This phenomenon is a saponification effect due to excessive use of NaOH in adjusting the pH during the study. The residual oil undergoes hydrolysis with NaOH to produce glycerol and fatty acid salts called soap, which is more soluble in water than in organic solvent. The effects of pH on sorption capacity for each derivative are shown in Fig. 5.

Effect of mixing time: The influence of contact time for each sorbent is shown in Fig. 6. Chitosan and oleoyl chitosan required 30 min to achieve the maximum sorption capacity of

Fig. 5. Sorption capacity of sorbent against pH samples

Fig. 6. Sorption capacity of sorbent against contact time

the residual oil. The breakage of oil droplets was greatly enhanced by the agitation process, thus reducing the diameter of oil droplets (emulsification), creating more interfacial areas available for the sorption process [6]. In contrast, N-methylene phosphonic chitosan and oleoyl methylene phosphonic chitosan required only 15 min to achieve the optimum sorption capacity. Exposing sorbent for a longer period may cause the derivatives to dissolve more in water.

Effect of initial concentration: The influence of initial concentration for each sorbent is shown in Fig. 7. The sorption capacity was increased when the concentration of residual oil was added. In fact, an increasing amount of residual oil (molecule per unit volume) will enhance more sorption to occur between the sorbent and residual oil. The sorption capacity of all the chitosan and its derivatives will increase until it reaches saturation levels.

Conclusion

Chitosan derivative namely oleoyl chitosan is chosen as one of the best sorbents compared to pure chitosan, oleoyl methylene phosphonic chitosan and methylene phosphonic chitosan for the sorption of residual oil. The optimum sorption capacity of residual oil by oleoyl chitosan was achieved at broader pH values due to the presence of the oleoyl group, which led to the interaction between the oleoyl group and hydrophobic

Fig. 7. Sorption capacity of sorbent against percentage of initial concentration

part of the residual oil. Oleoyl chitosan is suitable as a sorbent not only because it has the highest sorption capacity, but because it is also a non-toxic chitosan derivative. It can be used as a sorbent in the column sorption to remove the residual oil from palm oil refinery factory effluent without altering the original pH of the sample.

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