

Removal of Residual Oil from Palm Oil Mill Effluent by Novel Adsorbent of Alginate and Mangrove Composite Beads Coated by Chitosan

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Abstract: In this study, a novel adsorbent was prepared in bead shape which is Alginate and Mangrove Composite Beads Coated by Chitosan (AMCBCC) and well performed to remove residual oil from Palm Oil Mill Effluent (POME) using batch adsorption studies by different parameters: pH, adsorbent dosage, contact time and initial concentration. It was found that the maximum removal percentage of residual oil was 98.47% occurred at pH 3, 50 g/L of AMCBCC concentration and a contact time of 2.5 hrs. The adsorbent was characterized by Fourier Transform Infrared Spectroscopy (FTIR) to reveal the effective functional groups and to prove the successful coating by Chitosan and was also characterized by Scanning Electron Microscope (SEM) before and after the adsorption to provide an evidence that the residual oil had been adsorbed on the surface of the beads. These results indicated that AMCBCC demonstrate a potential application to remove residual oil from industrial wastewater.

Key words: Mangrove bark • Alginate • Chitosan • Adsorption • Residual oil • Palm Oil Mill Effluent

INTRODUCTION

Palm oil is one of the main industries in Malaysia; increasing the production of this oil will lead to increase its wastewater, which is called Palm Oil Mill Effluent (POME), it is generated from three stages of Palm Oil production: Sterilization, Clarification & Purification and Hydro cyclone [1]. Approximately, the amount of POME which is generated from producing (1) ton of Palm Oil is (2.5) tons. In the year 2010 in Malaysia higher than (60) million tons of POME were produced from (421) mills [2]. POME is a thick brown liquid, it consist of the following: water (95 – 96) %, Total Solid (4 – 5) %, Oil & Grease (0.6- 0.7) % [3]. The presence of residual oil in POME can pollute the water source and cause harmful effects to all living creatures if it discharged without treatment because the ability of POME to form an oily layer on the water surface, which will decrease the light penetration and will subsequently have an effect on photosynthesis. Moreover, this oily layer reduces the transfer of oxygen from the air into the water, leading to minimized the level

of dissolved oxygen in water, which makes the marine living organism in a direct threat, whereby this dangerous threat moves to human from the food chain [4]. The residual oil in untreated POME in a serious level with an average of (9065) mg/L [5], which exceeds the permissible limits issued by the Department of Environmental (DOE) Malaysia which is (50) mg/L. The treatment of oil in POME is a big issue due to the fact that the oil in an emulsified shape with high stability and the presence of glycolipids and phospholipids make the oil recovery much harder [6]. In spite of the various techniques had been used to remove residual oil from POME, Adsorption process using natural adsorbents is very encouraging method for residual oil removal [7]. Limited studies had been conducted to treat POME by using natural materials as adsorbent in adsorption process.

In this study a novel type of adsorbent was prepared: Alginate-Mangrove Composite Beads Coated by Chitosan (AMCBCC) in beads shape, due to the fact that the beads are the best form of biopolymer adsorbent for pollutants removal in wastewater [8] and also the beads

are easy to separate from the wastewater after treatment and easy to regenerate. Mangrove bark is obtained from charcoal factory, Alginate is a biopolymer obtained from the cell walls of brown algae and Chitosan is a copolymer obtained from chitin, chitin is produced from arthropods. These materials are natural and contains effective functional groups such as (carboxylic, phenolic, hydroxyl) in Mangrove bark, (carboxylate and hydroxyl) in alginate and (hydroxyl and amino) in chitosan [9-11]. Among all these effective groups, amine has a great potential for adsorbing oil, due to the ability of amine to attract negative ions and bind the oil [12].

The main objective of this present research is to investigate the removal of residual oil from real POME using new type of adsorbent (AMCBCC). Various parameters were performed such as PH, dosage of adsorbent, contact time and initial concentration during the batch studies to explore the optimum parameters conditions.

MATERIALS AND METHODS

Materials: POME sample was collected from Palm Oil Mill in Seri Ulu Langat, Malaysia, the sample was left to cool and kept in a cooling room at about (4)°C. pH of POME was 4.9 and the oil content was (10843) mg/L.

Mangrove bark was collected from Charcoal factory in Kuala Sepetang Perak, Malaysia, Chitosan with medium molecular weight was obtained from local factory, Malaysia. All other chemicals (Na-alginate 99% purity, Acetic Acid, Calcium Chloride, Hydrochloric Acid, Sodium Hydroxide and Sulphuric Acid) were purchased from R&M Chemicals, Hexane was supplied from H&M Chemicals and Sodium Sulfate anhydrous was supplied from Bendosen Chemicals.

Preparation of Adsorbent: Mangrove bark was washed with distilled water, left to dry in room temperature, ground, sieved using 250 mesh sieve and treated by 0.1 M NaOH for (2) hours, due to the fact that NaOH is the best agent to improve the bark by increasing the active sites to get the maximum adsorption capacity [13]. Moreover, this modification was conducted to increase the hydrophobicity of the mangrove bark to adsorb residual oil [7, 14], then the bark was washed repeatedly with distilled water till the pH of solution became neutral, after that the bark filtered and dried in oven at (60-63)°C for 24 hrs. The treated bark was kept in glass container until used.

The mixture of Alginate and Mangrove bark (AM) was prepared by adding 5 g of Na-alginate into (200) ml of distilled water, then was continuously stirring till the Alginate completely dissolved, after that (2.5) g of the treated mangrove bark was added to the Na-alginate mixture and left to mix till it became homogenous. Using syringe pump device to form the Beads by dropping (AM) mixture into (0.2) M CaCl₂ solution and kept in the solution for 24 hours. The beads were washed with distilled water to remove the excess of CaCl₂, left to dry in room temperature then kept in glass container until used.

In order to coat the beads, Chitosan solution was prepared by adding (7.5) g of chitosan powder to (250) ml of (0.2%) acetic acid solution, kept stirring for (3) hours at (45-50)°C, to get the viscous gel [15], then the solution of chitosan was inserted in Ultra Sonic device for (10) min, after that the solution left in room temperature for 24 hours. (40)g of beads were immersed in (250)ml of chitosan solution with slow stirring at (45-50)°C for one hour, after that the beads were removed from chitosan solution and were immersed in (250) ml of (0.1) M NaOH for one hour to become neutralized with the excess acetic acid [15]. Finally, AMCBCC were washed with distilled water till the pH of the solution became neutral, left to dry in the room temperature and kept in glass container for further experiments.

Batch Adsorption Studies: The batch adsorption studies were achieved in series of 250 ml glass bottles, each one contain 200 ml of POME, a fixed amount of AMCBCC were added and agitated at 150 rpm at room temperature. The effects of different parameters were studied such as pH, dosage, contact time and initial concentration. The pH of POME solution was adjusted by using 0.1 M NaOH and 0.1 M HCl in the range of (3-9). The effect of dosage was conducted in the range of (2.5-20) g. The contact time was varied from (0.5-96) hours and the initial concentration was set by diluting the original raw POME to the range of (20%-80%) and the raw POME was considered to be 100%. The residual oil concentration in POME before and after the treatment were determined by Partition-Gravimetric Method in the standard recommended methods for the examination of water and wastewater [16]. In this method, the sample of POME was first acidified with 1:1 H₂SO₄ till the pH of the sample was equal or less than (2). The acidified sample was transferred to a separatory funnel and (30) ml of Hexane was added, then the separatory funnel was capped and shaken (60) times for about (2) minute with releasing the

pressure from time to time. The layer was left to separate for (5-15) minutes. The lower layer was discarded and the top layer was drained slowly into filter paper containing (1) g of anhydrous sodium sulphate placed in a funnel into a pre-weighted conical flask. Then, the conical flask with the collected sample was put in an oven at (70) °C until it was completely dried. The conical flask was cooled in a desiccator for (30) minutes and weighted. The residue oil concentration was calculated by using equation (1).

$$\text{Residual Oil (mg/L)} = \frac{(W2 - W1)}{V} \times 10^6 \quad (1)$$

where: W1 and W2 are the initial and final weight respectively of the conical flask (g), V is the volume of the sample (ml).

The Removal Percentage of residual oil was calculated by using equations (2).

$$\text{Removal \%} = \frac{(C_i - C_e)}{C_i} \times 100 \quad (2)$$

where C_i and C_e (mg/L) are the initial and equilibrium concentration of the adsorbate respectively.

Characterization Studies: Fourier Transform Infrared Spectroscopy (FTIR) analysis was conducted using Perkin Elmer instrument, model spectrum 100 to reveal the main functional groups on AMCBCC, the spectra were measured from (4000 to 600) cm^{-1} . Scanning Electron Microscope (SEM) was used to determine the surface morphology of the adsorbent by using Hitachi instrument, the beads were coated with gold (Au) before the analysis to magnify the electron transmission.

Point of Zero Charge (pHzpc): Point of zero charge of AMCBCC was determined by solid addition method [17]. 50 ml of 0.01 M KNO_3 was added to a series of 100 ml capped glass bottle. The pH of these solutions in the bottles were adjusted from (2-11) using 0.1M KOH and 0.1 M HNO_3 . After that, (1) g of the AMCBCC was weighted and added to each bottle. The bottles were then closed and put in a shaker at 150 rpm for 5 days. Then, the mixture was filtered and the final pH of the solution was measured. After that, the ΔpH was computed using equation (3).

$$\Delta\text{pH} = \text{pH}_i - \text{pH}_f \quad (3)$$

where: pH_i and pH_f are the initial and the final pH of the solution.

A curve of pH_i against ΔpH was plotted, where the point in which the curve crosses the zero line was the point of zero charge pHzpc.

RESULTS AND DISCUSSION

Characterization of the Adsorbent: From Fig. (1), it is found that the main peak was at the wave number (3395.96) cm^{-1} , which referred to hydroxyl group, this group was presented in mangrove bark, alginate and chitosan [11, 14, 18]. The wave number (1642.59) cm^{-1} referred to carboxyl group, which was presented in alginate [19]. Moreover, the wave numbers (1034.87 and 779.23) cm^{-1} indicated to the functional group amine, which can be considered evident of coating by chitosan [7]. SEM images of beads before and after the adsorption are shown in Fig.2 (a, b). Fig.2.a depicts the image of beads before adsorption, which was in spherical shape and was contained unlimited numbers of holes on its surface, which led to the increase in the surface area. On the other hand the image of beads after the adsorption (Fig. 2.b) shows that the shape was still spherical and contained less holes, due to the fact that the beads after adsorption were covered with the residual oil.

Point of Zero Charge (pHzpc): Based on Fig.3, the pHzpc of AMCBCC was found to be (7.4), This meant that the surface of beads will have a positive charge when the initial pH of the solution is lower than the point of zero charge: contrariwise, the surface of the adsorbent will have a negative charge when the initial pH of the solution is higher than the point of zero charge [20].

Batch Adsorption Studies

The Effect of pH: The removal of residual oil was remarkably influenced by the value of pH, because the pH had a great impact on the emulsion stability via controlling the degree of ionization of the residual oil [6]. Fig. 4 illustrates the effect of pH on the removal of residual oil and it is shown that the highest removal percentage of residual oil 94.12% was obtained at pH 3, due to the fact that the acidic solution forced the oil droplets to break and the emulsion to separate, which improved the removal of oil and also in this acidic solution the amine groups of the beads tend to protonate and lead to increase the electrostatic attraction between the effective adsorption sites and residual oil [21]. Moreover, at this pH, which is lower than pHzpc (7.4), the surface of the beads became a positive charge and could attract the

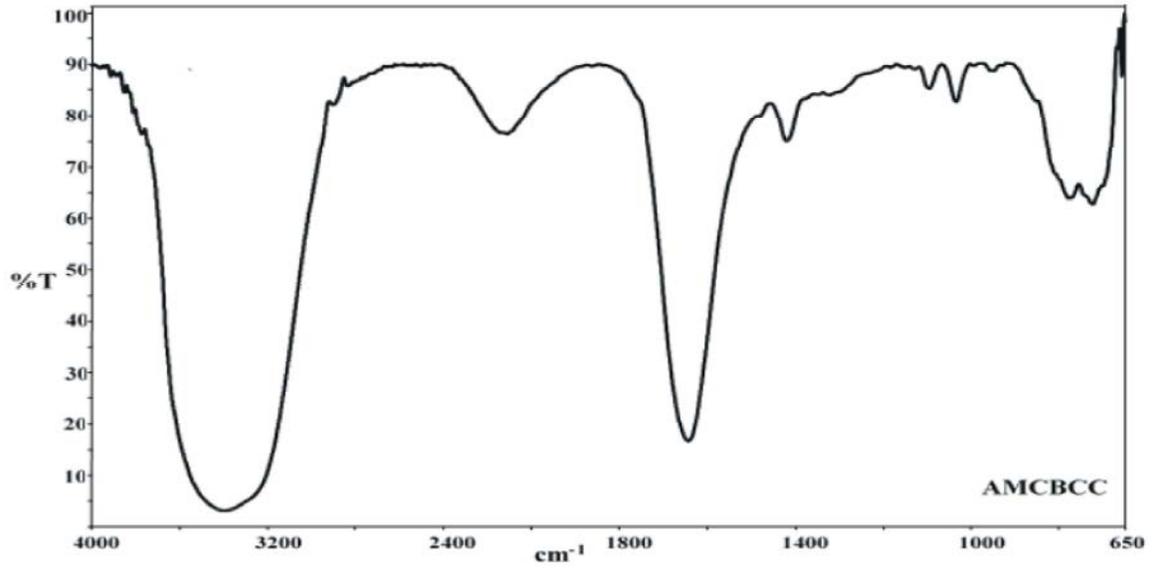


Fig. 1: FTIR spectra of AMCBCC

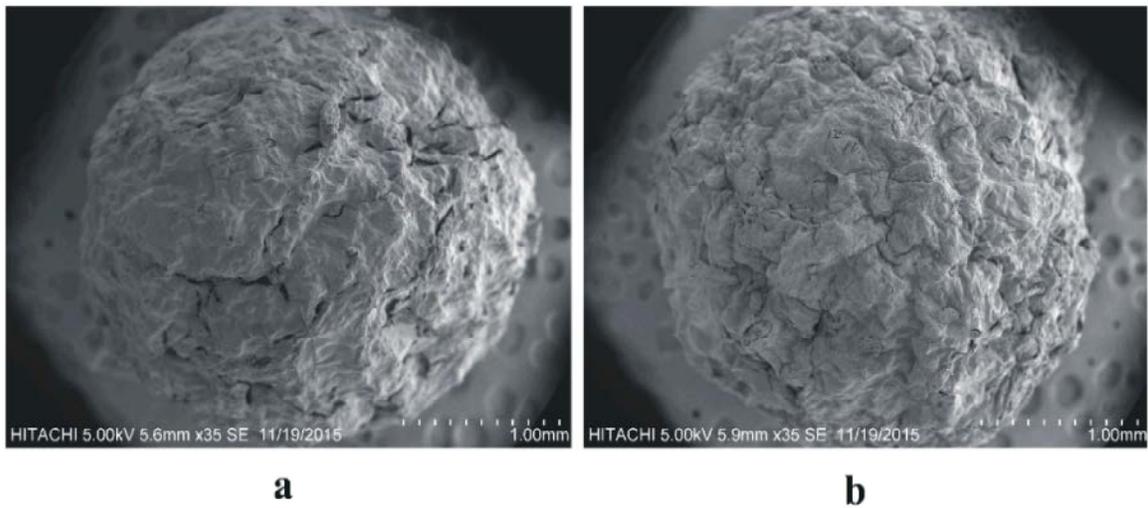


Fig. 2: SEM of: (a.) AMCBCC before adsorption and (b) AMCBCC after adsorption

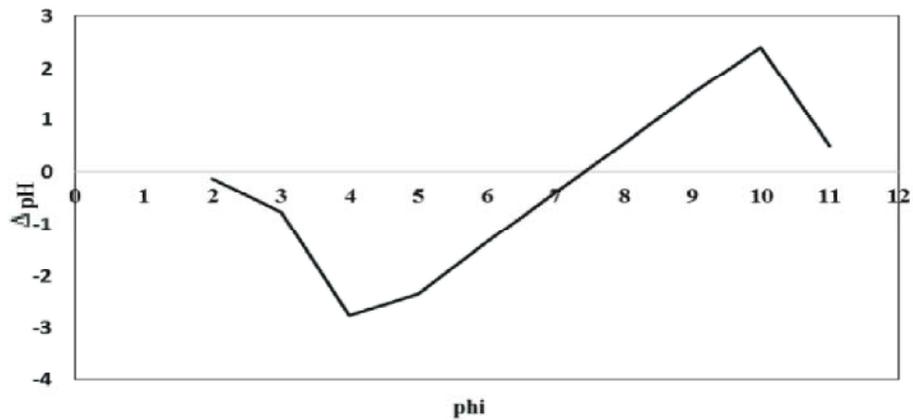


Fig. 3: Point of Zero Charge of AMCBCC

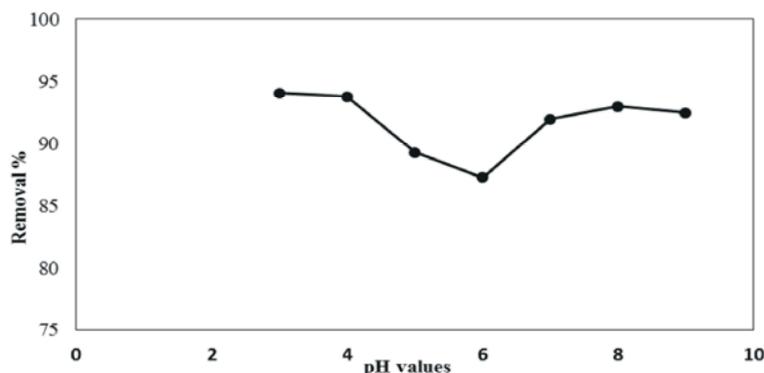


Fig. 4: The Effect of pH on the Removal of Residual Oil using AMCBCC

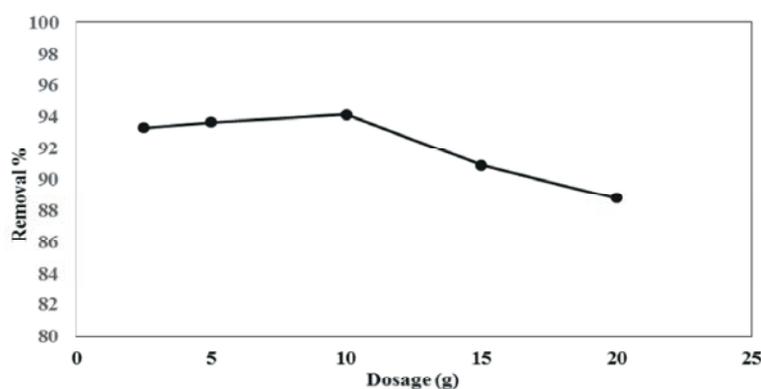


Fig. 5: The Effect of Adsorbent Dosage on the Removal of Residual Oil using AMCBCC

residual oil which is negatively charge in POME. Meanwhile, the removal percentage decreased and reached to the lowest level at pH 6, which was (87.3%), this trend was identical to the adsorption of residual oil in a previous studies [21, 22], then it increased once again at pH 7-9 with the removal percentage of 92%- 92.5% respectively and this can be explained as at a higher pH the process of saponification occurred, in order to reach this higher values of pH, NaOH was added to POME and this NaOH reacted with the oil to produce glycerol and fatty acid salts called soap, which is more soluble in water than in Hexane [7].

The Effect of Adsorbent Dosage: Fig. 5 illustrates the effect of adsorbent dosage on the removal of residual oil and it is shown that the removal percentage increased when the dosage of AMCBCC increased and reached the highest removal of 95.75% at the dosage of 10 g, because of increasing the adsorbent dosage led to the increase the binding site especially amine groups which is positively charged and could help to adsorb and coagulate the negatively charged residual oil [22]. Moreover, it led to increase the modified mangrove bark which is

hydrophobic surface and help to adsorb residual oil. On the other hand, when the dosage increased over 10 g, the removal decreased and reached 88.8% at dosage 20 g, because of further increasing in dosage led to a lower charge density of adsorbent whereby this could not destabilize the oil droplets [12].

The Effect of Contact Time: The effect of contact time on the removal of residual oil is illustrated in Fig. 6, where by increasing the contact time, the removal percentage increased till it reached the equilibrium at 2.5 hours, with the highest percentage removal of 98.47%.

It can be noticed that the removal percentage of residual oil rapidly increased through the first 2.5 hours, due to the presence of the adsorption sites, as well as the higher adsorption driving force that led to the increase of the removal percentage of residual oil [6]. Moreover, this highest removal percentage occurred at this time, because this was the best time to break the oil droplets as shown in Fig. 7(a) which illustrates that after 3 hours the oil droplets had broken, while in Fig. 7(b) after 12 hours, the oily particles agglomerated to form balls and the colour of POME also changed to be much lighter. This oily ball may

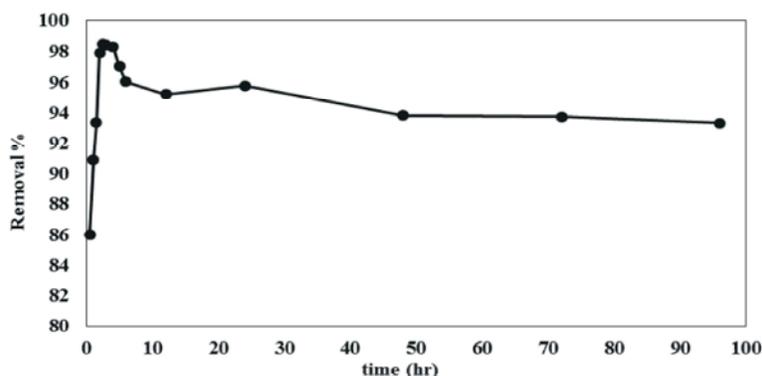


Fig. 6: The Effect of Contact Time on the Removal of Residual Oil using AMCBCC

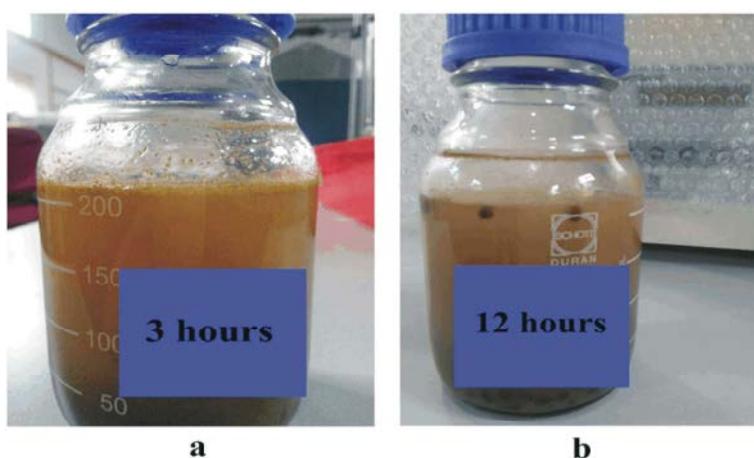


Fig. 7: The Effect of Contact Time after the Adsorption a. after 3 hrs. b. after 12 hrs

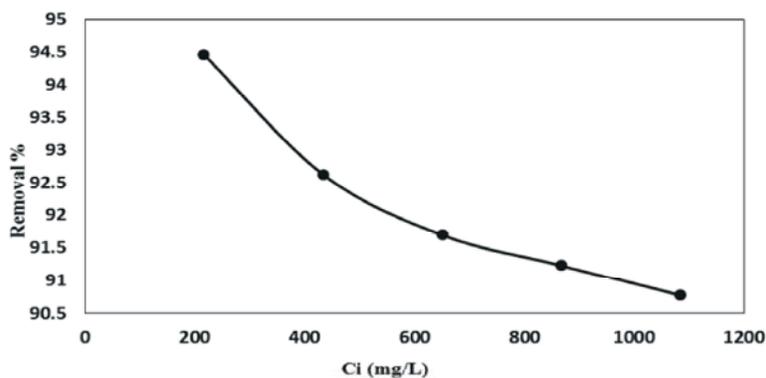


Fig. 8: The Effect of Initial Concentration on the Removal of Residual Oil using AMCBCC

be produced from binding the residual oil which was effected from the amine group, because the amine is a positive charge at an acidic solution and supports the oil in POME which is a negative charge to coagulate and adsorb till it is neutralized. Then, the small particles interact with each other [22]. This oily ball did not become a sediment and kept floating on the surface of the treated POME, because it is produced

from oil and oil has less density than water. In this research, the mixing speed was fixed at 150 r.p.m and did not transfer to slow stirring and as a result the oily balls did not turn to bigger balls and kept floating and then was removed by filtration. This means that the beads did not only adsorb the residual oil but also agglomerated it due to the effective function group amine.

The Effect of Initial Concentration: The effects of initial concentration on the removal of residue oil is illustrated in Figure 7. It can be noticed that by increasing the initial concentration the removal percentage decreased, due to the fact that at lower concentrations, most of the residual oil was adsorbed by AMCBCC, while at higher concentrations the AMCBCC were rapidly saturated by residual oil [23].

CONCLUSIONS

In this research, AMCBCC were prepared by mixing alginate and base modified mangrove bark to form beads then coated by chitosan and well performed for residual oil removal from POME and were advantageous from their effective functional groups and from the hydrophobic surface of modified mangrove bark. The SEM results revealed that the beads after the treatment were influenced due to the adsorption of residual oil. The maximum removal percentage obtained was above 90 % at pH 3, 10 g of AMCBCC dosage at 2.5 hours and when the initial concentration increased, the removal percentage decreased.

This research suggested that Alginate-Mangrove Composite Beads Coated by Chitosan (AMCBCC) is a promising adsorbent and coagulant to remove residual oil from industrial wastewater.

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