

ADSORPTION OF HEAVY METALS AND RESIDUAL OIL FROM PALM OIL MILL EFFLUENT USING A NOVEL ADSORBENT OF ALGINATE AND MANGROVE COMPOSITE BEADS COATED WITH CHITOSAN IN A PACKED BED COLUMN

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ABSTRACT: In this study, a novel adsorbent was prepared, namely alginate and mangrove composite beads coated with chitosan (AMCBCC), and performed well to remove heavy metals and residual oil from palm oil mill effluent (POME) using continuous adsorption studies in a fixed bed column under different bed heights. Thomas and Yoon–Nelson models were applied to predict the breakthrough curve and to compute the characteristic parameters such as maximum capacity and the time required for 50% of adsorbate breakthrough. It was found that the total removal percentage of iron ions, zinc ions, and residual oil were 26.75%, 76.74%, and 83% respectively at pH 3, and a bed height 27 cm. Both models can well describe the breakthrough curve of heavy metals and residual oil. These results indicated that AMCBCC can be used to remove heavy metals and residual oil from industrial wastewater.

ABSTRAK: Kajian ini menyediakan tentang penjerap baharu iaitu alginat dan manik komposit bakau bersalut kitosan (AMCBCC), berfungsi menyingkirkan logam berat dan sisa minyak daripada efluen kilang minyak sawit (POME) dengan sempurna, menggunakan kajian penjerapan berterusan dalam lapisan lajur tetap pada ketinggian berbeza. Model Thomas dan Yoon-Nelson telah digunakan bagi meramal lengkungan terbaik dan mengira parameter cirian seperti keupayaan maksimum dan tempoh diperlukan bagi 50% lengkungan terbaik penjerap. Jumlah peratusan penyingkiran ion besi, ion zink, dan sisa minyak masing-masing sebanyak 26.75%, 76.74%, dan 83% pada pH 3, dan pada ketinggian lapisan 27 cm. Kedua-dua model mampu menggambarkan lengkungan terbaik bagi logam berat dan sisa minyak dengan sempurna. Dapatan ini menunjukkan AMCBCC sesuai digunakan bagi menyingkirkan logam berat dan sisa minyak daripada air sisa industri.

KEYWORDS: *continuous adsorption; heavy metals; residual oil; palm oil mill effluent; adsorbent*

1. INTRODUCTION

The palm oil industry is considered to be a major industry and a key contributor to economic prosperity in Malaysia. A huge amount of effluent is discharged during the palm oil production process, which is known as palm oil mill effluent (POME).

POME is a thick brown liquid owing to the presence of lignin, humic acid, lipids, fatty acids, and tannin [1]. It is hot with a temperature between 80 °C and 90 °C and acidic with a pH of 4.5–5 [2]. POME is oily wastewater mainly consisting of the following: water 95% - 96%, total solid 4% - 5%, and oil and Grease 0.6% - 0.7% [3]. The presence of residual oil in POME can pollute water sources and cause harmful effects to all aquatic creatures if it is discharged without treatment because POME has the ability to form an oily layer on the water surface. This reduces the light penetration into the water and subsequently has an adverse effect on photosynthesis. Moreover, this oily layer decreases the transfer of oxygen from air to water, leading to a low level of dissolved oxygen in water. This creates a direct threat to marine living organisms, which in turn leads to adverse effects on humans through the food chain [4]. The residual oil content in untreated POME is very high, at an average of 9065 mg/l [5], which exceeds the permissible limits issued by the Department of Environmental (DOE) Malaysia (50 mg/l). Moreover, POME contains many heavy metals in critical levels such as iron and zinc. Iron ions have the highest concentration and are found at a dangerous levels in POME with an average of 119.5 mg/l [6], which exceeds the permissible limits (5 mg/L) issued by DOE Malaysia. Heavy metals are non-biodegradable, toxic, and bio-accumulate in aquatic living organisms. They can also be transferred to humans through the food chain, and can cause many diseases such as cancer [7-8]. Untreated POME causes severe water and soil pollution. It changes the water to brown, stinky, and slimy, which may eliminate living marine organisms and also endanger the planet in the case of discharging POME on land [9-10]. Although various methods have been used for the treatment of effluents containing heavy metals and residual oil, the adsorption process using natural adsorbents is a very encouraging method for pollutant removal [11]. A continuous adsorption process is very applicable to the batch adsorption process because a continuous process is cost-effective, feasible, requires less amount of adsorbent, and can be controlled [12]. Limited studies have been conducted on the treatment of POME using natural materials as adsorbents by a continuous adsorption process.

In this study, a novel type of adsorbent was prepared. It is known as alginate-mangrove composite beads coated with chitosan (AMCBCC). The adsorbent is in the shape of beads, which is the best form of biopolymer adsorbent for the removal of pollutants in wastewater, and also to prevent column clogging problems [13]. In addition, it is easy to separate the beads from the wastewater after treatment and they can also be easily regenerated. Mangrove bark is obtained from charcoal factories, alginate is a biopolymer obtained from the cell walls of brown algae, and chitosan is a copolymer obtained from chitin, which is produced from arthropods. These materials are natural and contain effective functional groups such as carboxylic, phenolic, and hydroxyl in mangrove bark, carboxylate and hydroxyl in alginate, and hydroxyl and amino in chitosan [14-16]. These functional groups are well known of their ability to remove pollutants from industrial wastewater [17].

The main purpose of the present research was to remove heavy metals and residual oil from actual POME using a new type of adsorbent (AMCBCC) by continuous adsorption studies in a fixed bed column under different bed height. Moreover, two kinetic models Thomas and Yoon-Nelson were also conducted in this work.

2. MATERIALS AND METHODS

2.1 Materials

A sample of POME was collected from a palm oil mill in Seri Ulu Langat, Malaysia. The sample was left to cool and kept in a cooling room at about 4 °C. The characteristics of the sample are specified in Table 1.

Mangrove bark was obtained from a charcoal factory in Kuala Sepetang, Perak, Malaysia, and chitosan with a medium molecular weight was obtained from a local factory in Malaysia. The other chemicals (sodium alginate ~98.5%, acetic acid 99.8%, nitric acid 65%, calcium chloride 99.5%, hydrochloric acid 37%, sodium hydroxide 99%, and sulphuric acid ~95%) were purchased from R&M Chemicals. Hexane was supplied from H&M Chemicals, and sodium sulfate anhydrous ~99% was supplied from Bendosen Chemicals.

Table 1: Characteristics of raw POME sample

Characteristics	Values
Oil and grease	10843 mg/l
COD	42240 mg/l
Fe	103.3 mg/l
Zn	7.5 mg/l
pH	4.9

2.2 Preparation of the Adsorbent

The mangrove bark was washed with distilled water, dried at room temperature, ground, and sieved using a 250-mesh sieve. It was then treated by 0.1 M NaOH for 2 hours, as NaOH is the best agent for improving the bark by increasing the active sites to obtain the maximum adsorption capacity [18]. Moreover, this modification was conducted to increase the hydrophobicity of the mangrove bark to adsorb residual oil [11-19]. Next, the bark was washed many times with distilled water until the pH of the solution became neutral. After that, the bark was filtered and dried in an oven at 60-63 °C for 24 hrs. The treated bark was kept in a glass container for later use.

The mixture of alginate and mangrove bark (AM) was prepared by adding 5 g of sodium alginate into 200 ml of distilled water. The mixture was then stirred continuously until the alginate had completely dissolved. Next, 2.5 g of the treated mangrove bark was added to the sodium alginate solution and mixed together until they became homogenous. A syringe pump device was used to form the alginate-mangrove composite beads (AMCB) by dropping the alginate-mangrove mixture into a solution of 0.2 M CaCl₂. The beads were kept in the solution for 24 hrs before being washed with distilled water to remove the excess CaCl₂. They were then left to dry at room temperature and kept in a glass container for later use.

To coat the beads, a chitosan solution was prepared by adding 7.5 g of chitosan powder to 250 ml of 0.2% acetic acid solution. The mixture was stirred continuously for 3 hrs at 45-50 °C to obtain a viscous gel [20]. Then, the chitosan solution was inserted into an ultrasonic device for 10 mins, after which, the solution was left at room temperature for 24 hrs. 40 g

of AMCB was immersed in 250 ml of chitosan solution and then stirred slowly at 45-50 °C for one hour. Next, the beads were removed from the chitosan solution and were immersed in 250 ml of 0.1 M NaOH for one hour to neutralise the excess acetic acid [20]. Finally, AMCBCC was washed with distilled water until the pH of the solution became neutral. It was then left to dry at room temperature and kept in a glass container for further experimentation.

2.3 Characterization Studies

Fourier transform infrared spectroscopy (FTIR) was used to determine the surface functional groups in the AMCBCC, where the spectra were measured from 4000 to 600 cm^{-1} . The physical characteristics were checked for the beads to determine the weight and size of each bead.

2.4 Column Adsorption Studies

Continuous studies for the removal of heavy metals and residual oil from POME were performed in a fixed bed column packed with AMCBCC (Fig. 1). The glass column was 40 cm long and 1.9 cm in diameter.

The continuous studies were performed by studying the effects of bed height (9, 18, and 27 cm) at a constant pH obtained from the batch studies and at a constant flow rate of 3 ml/min, which was the lowest flow rate of this device. Based on the previous studies, it was revealed that at the minimum flow rate, a shorter breakthrough curve can be found [12, 21-22]. In order to do the experiment, the POME was acidified to pH 3 and put in the storage tank. The column was packed with AMCBCC until it reached the required height, and then the flow rate was set 3 ml/min. The adjusted POME was then pumped through the fixed bed of AMCBCC. At regular intervals, the sample of treated POME was collected and prepared to be analyzed to determine the heavy metals and residual oil. The experiments were performed for about 540 min.

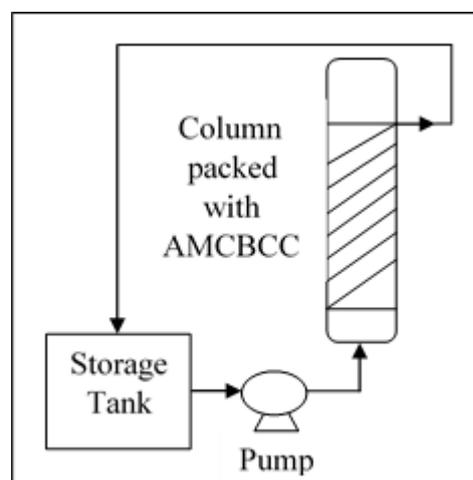


Fig. 1 Schematic diagram of adsorption column.

2.5 Analytical Techniques

2.5.1 Determination of Heavy Metals

The metals concentration in POME before and after treatment were determined using an inductively coupled plasma optical emission spectrometer (ICP-OES). In order to

execute the test, the samples were filtered using filter paper and acidified by adding concentrated amount of HNO₃ to prevent the precipitation of heavy metals [13]

2.5.2 Determination of Residual Oil

The amount of residual oil in POME before and after the treatment was determined using the Partition-Gravimetric method, a standard recommended method for the examination of water and wastewater [23]. In this method, the sample of POME was first acidified with 1:1 H₂SO₄ until 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 to the sample in the separatory funnel. The separatory funnel was capped and shaken 60 times for about 2 minutes while releasing the pressure from time to time. The layer was left to separate for 5-15 minutes. The lower layer was discarded. Then, the top layer was drained slowly into filter paper containing 1g of anhydrous sodium sulphate placed in a funnel into a pre-weighted conical flask. The conical flask with the collected sample was then 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 residual oil concentration was calculated using equation (1):

$$\text{Residual Oil (mg/L)} = \frac{(W_2 - W_1)}{v} \times 10^6 \quad (1)$$

Where: W_1 and W_2 are the initial and final weight of the conical flask, respectively (g), and v is the volume of the sample (ml).

2.6 Mathematical Equation of the Fixed Bed Column in Continuous Studies

The most important factor in the fixed bed column is the breakthrough curve, which is usually obtained from plotting a curve between $\left[\frac{C_t}{C_i}\right]$ versus the contact time (t), where C_i and C_t are the inlet and outlet adsorbate concentration (mg/l) [12]. The total adsorbed adsorbate in the column (q_{total}) is determined using equation (2):

$$q_{total} \text{ (mg)} = \frac{Q A}{1000} \quad (2)$$

Where: q_{total} is the total metal ions or residue oil adsorbed quantity (mg). Q is the volumetric flow rate (ml/min), and A is the area under the curve which is determined from plot of the adsorbed concentration (C_{ad}) versus time (t).

$$A = \int_{t=t_{initial}}^{t=t_{total}} C_{ad} dt$$

Where: C_{ad} is the adsorbed concentration (mg/l) obtained from $(C_i - C_t)$.

The equilibrium adsorbate uptake ($q_{e.exp}$) is calculated using equation (3):

$$q_{e.exp} \text{ (mg/g)} = \frac{q_{total}}{X} \quad (3)$$

Where: X is the total dry weight of absorbent (AMCBCC) in column (g)

The total amount of metal ions or oil sent to the column (M_{total}) is evaluated using equation (4):

$$M_{total} \text{ (mg)} = \frac{C_i Q t_{total}}{1000} \quad (4)$$

The unadsorbed concentration at equilibrium of metal ions or oil (C_{eq}) is obtained by equation (5):

$$C_{eq} = \frac{M_{total} - q_{total}}{v_{eff}} \times 1000 \quad (5)$$

Where: V_{eff} is the volume of effluent (ml) = $Q \times t_{total}$

The total removal percentage of metal ions or oil (Y) is the ratio of the total capacity (q_{total}) to the total amount of metal ions and oil sent to the column (M_{total}) can be obtained from equation (6):

$$Y = \frac{q_{total}}{M_{total}} \times 100 \quad (6)$$

2.7 Modeling of the Fixed Bed Column

In this research, the description of the breakthrough behavior of iron ions, zinc ions and residual oil on the AMCBCC and the characteristic parameters K_{Th} , q_x , K_{YN} , and \bar{U} were determined by two well-known models: the Thomas model and the Yoon-Nelson model.

2.7.1 Thomas Model

The Thomas model is designed to determine the maximum capacity of adsorption, which is one of the most important factors for column design. This model is also used in the description of the breakthrough curve of the column [12-21]. The linearized form of the Thomas equation is illustrated in equation (7):

$$\ln \left[\frac{C_i}{C_t} - 1 \right] = \frac{K_{Th} q_x m}{Q} - K_{Th} C_i t \quad (7)$$

Where: C_i and C_t are the inlet and outlet adsorbate concentration respectively (mg/l), Q is the volumetric flow rate (ml/min), t is the contact time (min), m is the mass of adsorbent (g), k_{Th} is Thomas kinetic coefficient (ml/min.mg), q_x is the maximum adsorption capacity (mg/g). With plot $\ln \left[\frac{C_i}{C_t} - 1 \right]$ versus t from the slope and the intercept, values of K_{Th} and q_x are determined.

2.7.2 Yoon-Nelson Model

This model is developed based on the assumption of adsorption and breakthrough of adsorbate probability [12]. It is less complicated and needs fewer parameters than the other models; moreover, it is usually used to determine the time required for 50% of the adsorbate breakthrough (\bar{U}). The linearized form of Yoon-Nelson equation is illustrated in equation (8):

$$\ln \frac{C_t}{C_i - C_t} = K_{YN} t - K_{YN} \bar{U} \quad (8)$$

Where: K_{YN} is the Yoon-Nelson rate of constant min^{-1} , \bar{U} is the time required for 50% of adsorbate breakthrough min, and t is the contact time min. Plot $\ln \frac{C_t}{C_i - C_t}$ versus t is to determine the slope and the intercept, and from the slope and the intercept, the values of K_{YN} and \bar{U} are calculated.

3. RESULTS AND DISCUSSION

3.1 Characterization of AMCBCC

From Fig. 2, it can be seen that the main peak was at the wave number of 3395.96 cm^{-1} , which refers to a hydroxyl group. This group was present in the mangrove bark, alginate, and chitosan [16, 24-25]. The wave number 1642.59 cm^{-1} refers to a carboxyl group, which was present in the alginate [26]. Moreover, the wave numbers 1034.87 and 779.23 cm^{-1}

indicate the amine functional group, which can be considered as evidence of the coating by chitosan [27]. The physical characteristics of one bead are 0.0715 g weight, and 2.89 mm diameter. Figure 3 shows image of the AMCBCC bead.

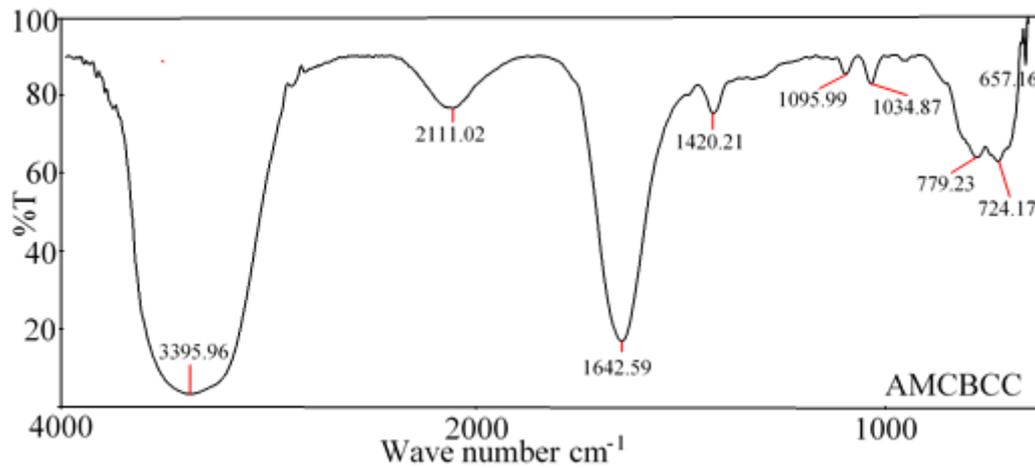


Fig. 2: FTIR spectrum of AMCBCC.



Fig. 3: Image of AMCBCC.

3.2 Effects of the Bed Height

The breakthrough curve of iron ions, zinc ions, and residual oil at different bed height are illustrated in Figs. 4, 5, and 6 respectively.

It is shown in Figs. 4, 5, and 6 that by increasing the bed heights from 9 cm to 27 cm, a slower breakthrough curve occurred and the adsorbent (AMCBCC) needed a longer time to reach the exhaustion point (which was the point where the outlet concentration was equal to the inlet concentration). The explanation for this can be that increasing the adsorbent led to more available binding sites, more contact time, and more surface area [28]. On the contrary, decreasing the bed height led to a faster breakthrough curve and less time to reach the exhaustion point, and this trend had been reported in other research [29]. The mathematical characterization of the column parameters for iron ions, zinc ions, and residual oil can be seen in Table 2.

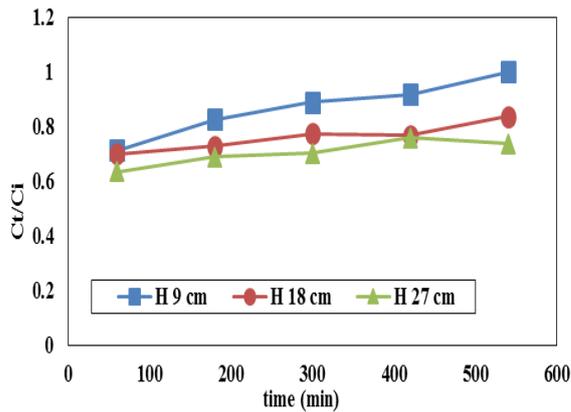


Fig. 4: Effect of the height on the adsorption of iron ions.

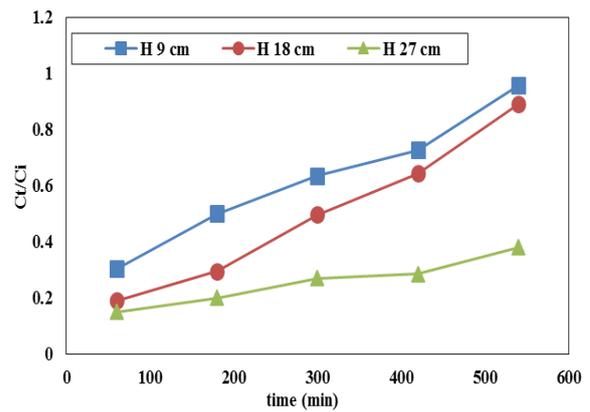


Fig. 5: Effect of the height on the adsorption of zinc ions.

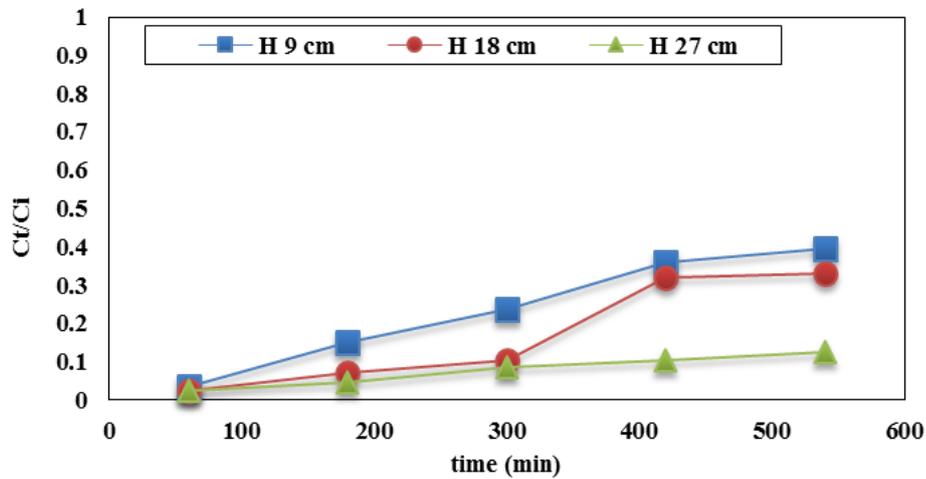


Fig. 6: Effect of the height on the adsorption of residual oil.

Table 2: Mathematical characterization of column parameters of iron ions, zinc ions, and residual oil at constant flow rate Q (3 ml/min)

Adsorbate	Bead height (cm)	q_{total} (mg)	M_{total} (mg)	$Y\%$	$q_{e.exp}$ (mg/g)	C_{eq} (mg/l)
Fe C_i (103.3) mg/l	9	17.09	167.30	10.20	0.95	92.72
	18	27.87	167.30	16.65	0.77	86.07
	27	44.75	167.30	26.75	0.83	75.66
Zn C_i (7.5) mg/l	9	4.33	12.15	35.60	0.24	4.80
	18	5.55	12.15	45.67	0.15	4.07
	27	9.32	12.15	76.74	0.17	1.74
Residual oil C_i (1084.3) mg/l	9	1366.45	1756.57	77.78	75.90	240.80
	18	1408.65	1756.57	80.20	39.13	214.76
	27	1458.49	1756.57	83.00	27.00	183.99

It can be noticed from Table 2 that by increasing the bed height from 9 to 27 cm, the total removal percentage ($Y\%$) increased from (10.20 to 26.75) % of iron ions, (35.60 to 76.74) % of zinc ions, and from (77.78 to 83.00) % of residual oil. On the other hand, by increasing the bed height, the unadsorbed equilibrium concentration of iron ions, zinc ions and residual oil decreased from (92.72 to 75.66) mg/l, (4.80 to 1.74) mg/l, and (240.80 to 183.99) mg/l respectively. Similar results were reported by a previous study [12].

3.2 Modeling of the Fixed Bed Column

3.3.1 Thomas Model

To obtain the parameters in the Thomas model, a plot of $\ln \left[\frac{C_i}{C_t} - 1 \right]$ versus time is illustrated in Figs. 7, 8, and 9 for iron ions, zinc ions, and residual oil respectively at different bed height, where the slope and the intercept of the linear equation were used to calculate the K_{Th} and q_x respectively, which are presented in Table 3. This model was applied to the range of $0.08 < \frac{C_t}{C_i} < 0.97$.

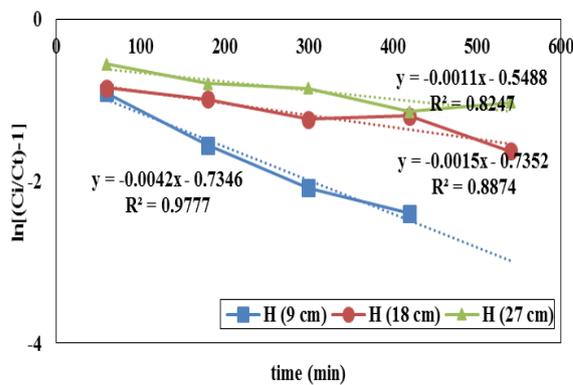


Fig. 7: Thomas model of iron ions at different bed heights.

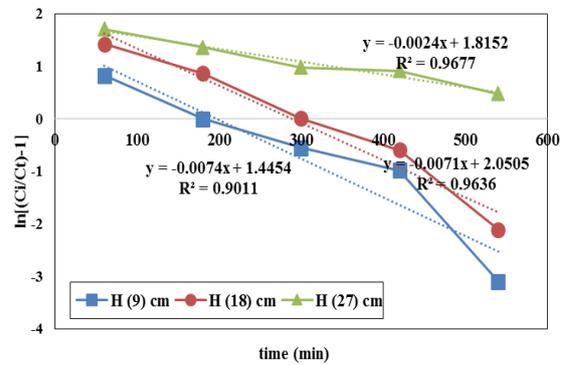


Fig. 8: Thomas model of zinc ions at different bed heights.

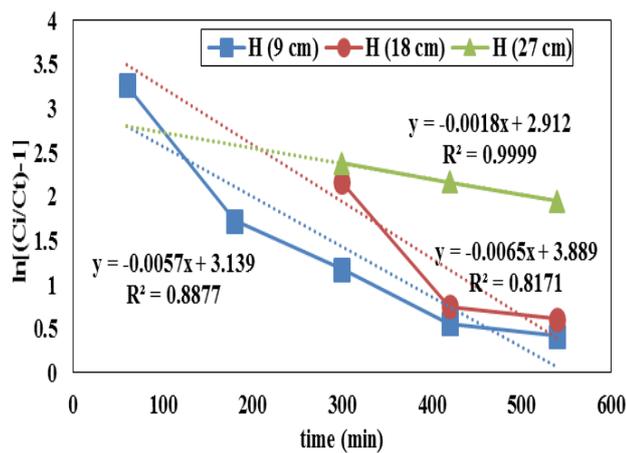


Fig. 9: Thomas model of residual oil at different bed heights.

It is shown in Table 3 that when the bed height was increased, the Thomas kinetic coefficient (K_{Th}) decreased, and this was a normal trend, as mentioned in a previous research [30].

Table 3: Mathematical characterization of Thomas model of iron ions, zinc ions and residual oil at constant flow rate Q (3 ml/min)

Adsorbate	m (g)	K_{Th} (ml/min.mg)	q_x (mg/g)	$q_{e.exp}$ (mg/g)	R^2
Fe <i>Ci</i> (103.3) mg/l	18	0.040	3.06	0.95	0.9777
	36	0.015	4.20	0.77	0.8874
	54	0.011	2.86	0.83	0.8247
Zn <i>Ci</i> (7.5) mg/l	18	0.98	0.25	0.24	0.9011
	36	0.94	0.18	0.15	0.9636
	54	0.32	0.32	0.17	0.9677
Oil & Grease <i>Ci</i> (1084.3) mg/l	18	5.26×10^{-3}	99.52	75.90	0.8877
	36	5.99×10^{-3}	54.15	39.13	0.8171
	54	1.66×10^{-3}	97.40	27.00	0.999

Figures 10, 11, and 12 illustrated that the Thomas model fitted better with zinc ions than with iron ions and residual oil, because the predicted values of zinc ions by the Thomas model were more agreeable with experimental values than for iron ions and residual oil. The values of R^2 from Table 3 also showed that Thomas models fitted better with zinc ions. Lastly, in comparison between the experimental $q_{e.exp}$ and the Thomas theoretical q_x for iron ions and residue oil, it was clear that there was a prominent difference between them, and this was a normal trend that was mentioned in a previous research [31]. On the other hand the values of $q_{e.exp}$ and q_x were in greater agreement for zinc ions.

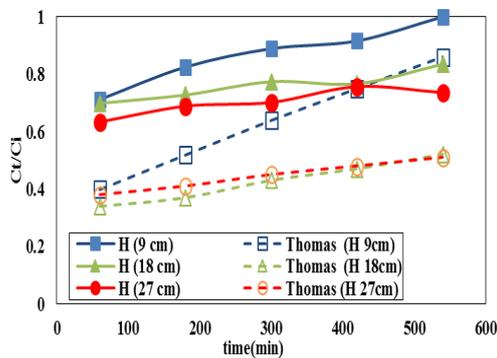


Fig. 10: Effect of bed height on iron ions removal predicted by Thomas model.

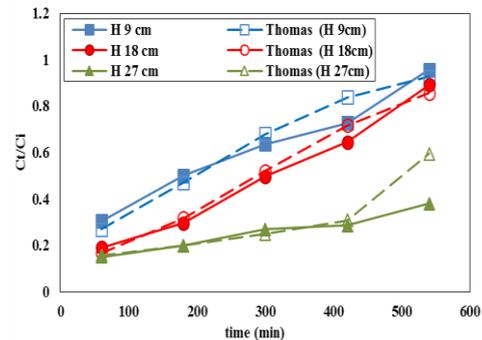


Fig. 11: Effect of bed height on zinc ions removal predicted by Thomas model.

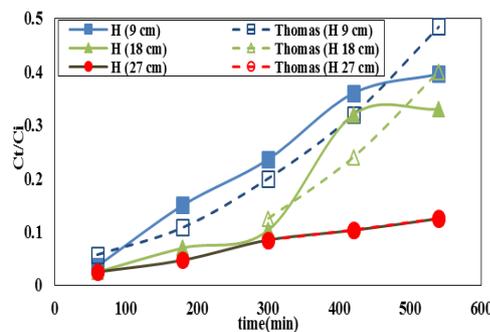


Fig. 12: Effect of bed height on residual oil removal predicted by Thomas model.

It is illustrated by Table 4 that by increasing the bed heights from 9 cm to 27 cm, the time required to reach 50% adsorbate breakthrough (T) increased from 174.92 min to 502.36 min, 196.60 min to 754.62 min, and from 550.70 min to 1617.94 min for iron ions, zinc ions, and residual oil, respectively. This trend had been reported in a previous study [32].

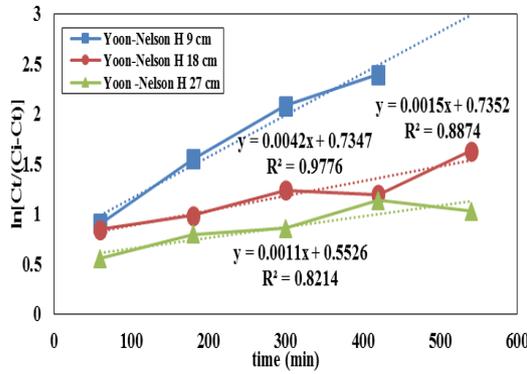


Fig. 13: Yoon-Nelson model of iron ions at different bed heights.

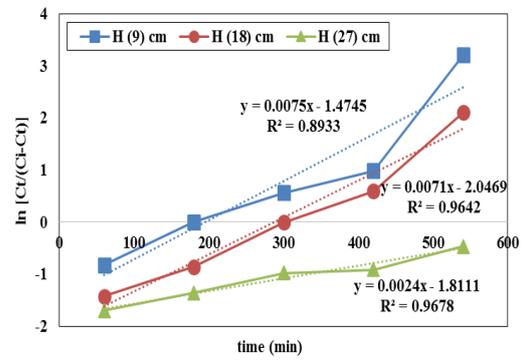


Fig. 14: Yoon-Nelson model of zinc ions at different bed heights.

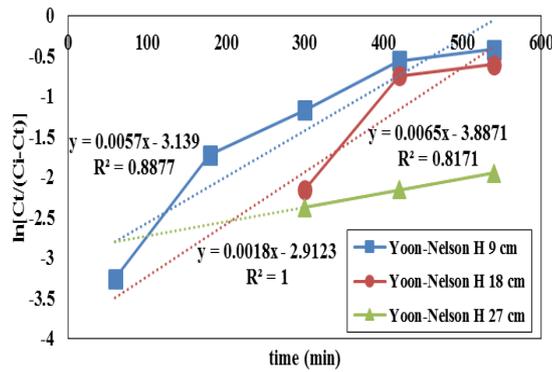


Fig. 15: Yoon-Nelson model of residual oil at different bed heights.

Table 4: Mathematical characterization of Yoon-Nelson of iron ions, zinc ions, and residue oil at constant flow rate Q (3 ml/min)

Adsorbate	H (cm)	$K_{YN}(1/min)$	T (min)	R^2
Fe C_i (103.3) mg/l	9	0.0042	174.92	0.9776
	18	0.0015	488.33	0.8874
	27	0.0011	502.36	0.8214
Zn C_i (7.5) mg/l	9	0.0075	196.60	0.8933
	18	0.0071	288.29	0.9642
	27	0.0024	754.62	0.9678
Residual oil C_i (1084.3) mg/l	9	0.0057	550.70	0.8877
	18	0.0065	598.01	0.8171
	27	0.0018	1617.94	1

Figures 16, 17, and 18 illustrated that the Yoon-Nelson model fitted better with zinc ions than with iron ions and residual oil because the predicted values by the Yoon-Nelson model of zinc ions were more agreeable with experimental values than for iron ions and residual oil. Moreover, the values of R^2 from Table 4 also showed that the Yoon-Nelson model fitted better for zinc ions.

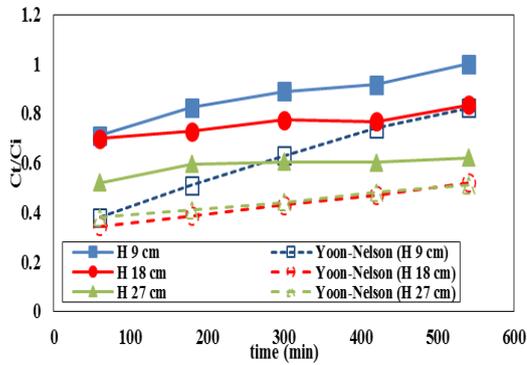


Fig. 16: Effect of bed height on iron ions removal predicted by Yoon-Nelson model.

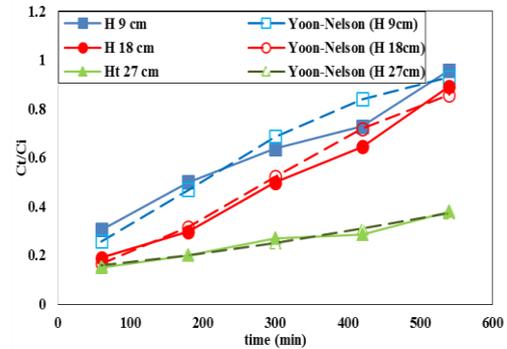


Fig. 17: Effect of bed height on zinc ions removal predicted by Yoon-Nelson model.

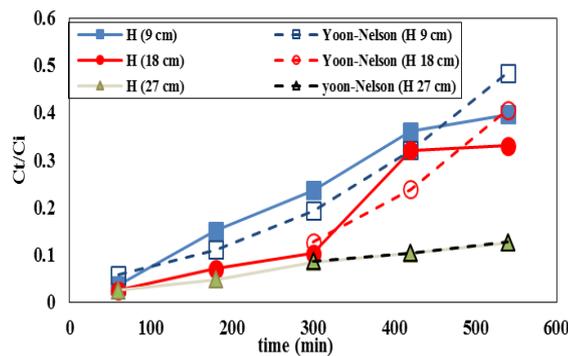


Fig. 18: Effect of bed height on residual oil removal predicted by Yoon-Nelson model.

4. CONCLUSION

In this work, the investigation of removal heavy metals and residual oil from POME was explored in a fixed bed column by a new type of adsorbent (AMCBCC). The adsorbent was characterized by FTIR to reveal the main functional groups in the beads. It was found that by increasing the bed heights from 9 cm to 27 cm, the adsorbent (AMCBCC) needed a longer time to reach the exhausted point. Moreover, by increasing the bed height, the removal percentage for iron ions, zinc ions and residual oil increased from 10.20 % to 26.75 %, 35.60 % to 76.74 %, and 77.78 % to 83.00 %, respectively. Furthermore, the Thomas model and the Yoon-Nelson model can both describe the adsorption of iron ions, zinc ions, and residual oil well, but the prediction data for both models are in greater agreement with the experimental data for zinc ions. Lastly, this research suggested that alginate-mangrove composite beads coated by chitosan (AMCBCC) are a promising adsorbent for the removal of heavy metals and residual oil from industrial wastewater.

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