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Removal of Colour from Palm Oil Mill Effluent Using Thermally Processed Dolomite: Batch Adsorption and Modelling Study

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ABSTRACT

Palm oil mill effluent is a significant wastewater generated during palm oil processing and is characterized by its dark brown colour due to high concentrations of recalcitrant organic compounds. Discharging untreated POME can disrupt aquatic ecosystems and environmental quality. Among alternative approaches, adsorption is widely recognised for its simplicity, affordability and effectiveness in pollutant removal. This study evaluates the effectiveness of thermally processed dolomite as an adsorbent for removing colour from POME through batch adsorption experiments. The dolomite was thermally treated at 800 °C for 6 hours. Experimental parameters were varied, including initial concentration (15 - 60% v/v), adsorbent dosage (2.5 - 12.0 g), contact time (15 - 240 minutes), and pH (4 - 10). Adsorption behaviour was then analysed using isotherm and kinetic models to investigate the underlying mechanism. Optimal conditions for colour adsorption were obtained at 15% (v/v) initial concentration, 5.0 g dolomite dosage, 180 minutes contact time and pH 7.5, achieving a maximum colour removal of 79.91%. The equilibrium data best aligned with the Langmuir isotherm (R^2 of 0.8467), indicating that adsorption occurred in a single layer on a uniform surface. Kinetic analysis showed a strong correlation with the pseudo-second-order model (R^2 of 0.9844), highlighting chemisorption as the dominant process. In conclusion, thermally processed dolomite is an efficient material for treating colour from POME and holds potential for sustainable wastewater treatment applications.

1. Introduction

Palm oil mill effluent (POME) is a concentrated industrial wastewater produced in large volumes throughout the palm oil milling operations. Malaysia, with more than 450 palm oil mills in operation, produces approximately 44 million tonnes of POME annually [1-2]. POME is characterized by a thick,

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brownish appearance and contains high concentrations of organic matter, including biochemical oxygen demand (BOD) of 25,000 mg/L, chemical oxygen demand (COD) of up to 51,000 mg/L, total suspended solids (TSS) of 18,000 mg/L and a low pH between 3.5 and 4.2 [3-4]. One of the most visually and environmentally concerning features of POME is its dark brown colour, which is primarily due to the presence of complex organic compounds such as tannins, lignin, and melanoidins formed during high-temperature sterilisation and oil extraction processes [5-7]. The coloured compounds in POME significantly reduce light penetration when discharged into water bodies, thereby limiting photosynthetic activity in aquatic plants and disturbing the ecological balance [8]. In addition, the coloured compounds in POME, particularly phenolic compounds can exert toxic effects on aquatic life and interfere with microbial activity in treatment systems. If discharged without adequate treatment, these compounds may degrade water quality, reduce biodiversity and pose potential health risks to communities that rely on river water for domestic and agricultural use [9].

Over the years, various treatment technologies have been developed to manage the environmental impact of POME, including biological, physical, and chemical methods. Among them, biological treatment using anaerobic ponding systems is the most common due to its ability to degrade organic matter under oxygen-free conditions. However, this method requires extensive land area, long retention times and proper monitoring to maintain efficiency [10-11]. Chemical treatments such as coagulation and flocculation are often used to enhance sedimentation of suspended solids but require constant chemical input and generate secondary sludge [12]. Physical processes like membrane filtration can produce high-quality effluent but suffer from high energy consumption, membrane fouling and costly maintenance [13-14]. More importantly, these conventional methods show limited efficiency in removing recalcitrant compounds such as tannins, lignin, and melanoidins, which are responsible for the intense colour of POME. These coloured compounds often remain in the effluent even after treatment due to their resistance to biodegradation, posing environmental risks when discharged. Consequently, the removal of colour from POME represents a significant challenge, requiring alternative approaches that are both efficient and sustainable.

Adsorption has emerged as a promising alternative for removing colour and other persistent contaminants. It involves the accumulation of molecules onto the surface of solid materials known as adsorbents. Its advantages include operational simplicity, reversibility, low cost and high efficiency in treating wastewater containing recalcitrant organic compounds [15]. The performance of adsorption is strongly influenced by the type of adsorbent employed. Numerous natural and affordable materials such as zeolites [16], clays [17], and agricultural wastes [18] have been widely investigated. Among these, dolomite is gaining interest due to its natural abundance, affordability and potential to remove various pollutants due to its porous structure and ion-exchange properties [19]. It consists mostly of calcium oxide (CaO), magnesium oxide (MgO) and carbon dioxide (CO_2) [20]. Thermal treatment or calcination of dolomite at temperatures between 800 - 1000 °C further enhances its surface area, porosity, and reactivity, making it more effective for adsorbing colour from wastewater [21]. These characteristics make thermally processed dolomite a promising, low-cost and sustainable solution for colour removal from POME.

Despite the growing interest in alternative materials for wastewater treatment, there is limited research on the use of thermally processed dolomite for the removal of colour from POME, particularly in the context of Malaysian dolomite sources. While previous studies have explored dolomite's application in removing heavy metals and other pollutants, few have focused specifically on its performance in treating colour compounds in complex effluents like POME. Addressing this gap is critical, as it could offer a cost-effective and sustainable solution for industries seeking to comply with discharge regulations and reduce environmental harm. Therefore, this study aims (1) to evaluate the influence of operating parameters such as initial POME concentration, adsorbent dosage, contact

time and pH on colour removal using thermally processed dolomite and (2) to analyse the adsorption mechanism through isotherm and kinetic modelling.

2. Methodology

2.1 Preparation of Adsorbent

Dolomite was used as the adsorbent in this study. Raw dolomite samples were obtained from Kangar Manufacturing Sdn. Bhd., Perlis, Malaysia. Initially, the dolomite was sieved to obtain particles with sizes below 300 µm using a motorized sieve shaker to ensure uniform particle size distribution. The sieved dolomite was then placed into ceramic crucibles and covered with lids to minimise contamination and oxidation during heat treatment. The crucibles were subsequently placed in a furnace and heated at 800 °C for a duration of 6 hours [20-21].

2.2 Collection of POME

POME samples were collected from the Setiakawan Kilang Kelapa Sawit factory, located in Kulim, Kedah, Malaysia. About 12 L of POME samples were collected directly from the end-of-pipe discharge point and stored in high-density polyethylene (HDPE) bottles. The date of the sampling was clearly labeled on each bottle. Then, the POME samples were placed in a laboratory chiller at 4 °C until further analysis to avoid change in the POME properties and preserve its quality [22].

2.3 Batch Adsorption Experiment

Adsorption studies were carried out under batch experiment to investigate how operational variables, namely initial concentration, adsorbent dosage, contact time and pH affect colour removal efficiency from POME using thermally processed dolomite. The tests were conducted in 250 mL Erlenmeyer flasks, each containing 100 mL of POME and agitated at 150 rpm using a rotary orbital shaker (SHO-2D, WiseShake, Korea) at room temperature [23]. The initial concentration of POME was adjusted by diluting raw POME with distilled water to simulate different effluent strengths. Specifically, POME was diluted to four different ratios: 15%, 20%, 40%, and 60% (v/v) [24], where the percentage indicates the volume of raw POME in 100 mL of total solution. The undiluted raw POME was considered as 100% concentration [25]. A fixed dolomite dosage of 5.0 g, a contact time of 60 minutes and a pH of 4.8 were used during these tests. Subsequently, the adsorbent dosage was varied (2.5 - 12.0 g) using the optimized initial POME concentration, while maintaining contact time and pH. The influence of contact time (15 - 240 minutes) was then assessed under optimized conditions. Finally, the effect of pH (4 - 10) was examined by adjusting the POME solution with NaOH or HCl. After each adsorption run, the solution was filtered to remove the dolomite and the colour concentration of the filtrate was measured using a DR 3900 spectrophotometer (Hach, USA), following the Platinum-Cobalt Standard Method 8025 at a wavelength of 455 nm. The percentage of colour removal (%R) was calculated by using Eq. (1) and the equilibrium adsorption capacity was calculated using Eq. (2).

$$\%R = \left(\frac{C_o - C_e}{C_o}\right) \times 100\% \quad (1)$$

where C_o and C_e refer to the initial and equilibrium concentration of colour (PtCo), respectively.

$$q_e = \frac{(C_o - C_e)V}{M} \quad (2)$$

where q_e is the equilibrium adsorption capacity (PtCo/g), V is the volume (L) and M is the weight of adsorbent (g).

2.4 Isotherms and Kinetics Modelling

The experimental data for colour adsorption was analyzed using the Langmuir and Freundlich isotherm models. The linear form of the Langmuir model is expressed as in Eq.(3) [26].

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{bq_{max}} \quad (3)$$

where C_e is the equilibrium concentration (PtCo), q_e is the amount adsorbed at equilibrium (PtCo/g), q_{max} is the maximum adsorption capacity (PtCo/g) and b is the Langmuir constant related to adsorption affinity (L/PtCo). The values of q_{max} and b were determined from the slope and intercept of the linear plot of C_e/q_e versus C_e. The Freundlich model was applied in the linear form and expressed as in Eq.(4) [27].

$$\log q_e = \log K_f + \frac{1}{n} log C_e \quad (4)$$

where K_f is the Freundlich constant (PtCo/g)(L/PtCo)$^{1/n}$ and n is the adsorption intensity. The constants K_f and n were obtained from the intercept and slope of the plot of log q_e versus log C_e.

The adsorption kinetics of colour removal were analyzed using three models: pseudo-first-order, pseudo-second-order and intraparticle diffusion. The pseudo-first-order model was applied in its linear form as in Eq.(5) [28].

$$log(q_e - q_t) = log\ q_e - \frac{k_1}{2.303} t \quad (5)$$

where q_t is the amount adsorbed at time t (PtCo/g), q_e is the equilibrium adsorption capacity (PtCo/g) and k_1 is the pseudo-first-order rate constant (1/min). The values of k_1 and q_e were determined from the slope and intercept of the linear plot of log ($q_e - q_t$) versus t. The pseudo-second-order model was expressed in its linear form as Eq.(6) [29].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

where k_2 is the pseudo-second-order rate constant (g/PtCo·min). The values of k_2 and q_e were obtained from the intercept and slope of the plot of t/q_t versus t. The intraparticle diffusion was examined using the Weber - Morris model given by Eq.(7) [30].

$$q_t = k_{id} t^{0.5} + C \quad (7)$$

where k_{id} is the intraparticle diffusion rate constant (PtCo/g·min$^{0.5}$) and C denotes the intercept associated with the boundary layer effect. All model parameters were calculated using linear regression and the coefficient of determination (R^2) was applied to assess how well each model fit the observed data.

3. Results and Discussion

3.1 Adsorption Study on Colour Removal

This section presents the findings on how operational parameters influence the colour removal efficiency of thermally processed dolomite during batch adsorption of POME. The parameters evaluated include initial POME concentration (represented as dilution ratios), adsorbent dosage, contact time and pH. These factors were varied to assess their individual effects on the adsorption process.

3.1.1 Effect of initial POME concentration

Table 1 shows the initial and final colour concentrations of POME at four different initial concentrations: 15%, 20%, 40%, and 60% (v/v). Figure 1 illustrates the effect of initial POME concentration on the percentage removal of colour and the corresponding uptake capacity of thermally processed dolomite. From Table 1, it can be observed that the colour concentration of POME decreased after adsorption at all tested concentrations. For example, at an initial POME concentration of 15% (v/v), the colour was reduced from 430 PtCo to 245 PtCo, while at 60% (v/v), the reduction was from 2454 PtCo to 2201 PtCo. The corresponding percentage removals are shown in Figure 1, where the highest removal efficiency of 43.02% was achieved at the lowest initial POME concentration (15% v/v) and this efficiency declined progressively to 10.34% at the highest concentration tested (60% v/v). These results revealed that increasing the initial concentration of POME led to a decrease in the percentage removal of colour. In contrast, the total amount of colour adsorbed per unit mass of adsorbent (PtCo/g) increased as the initial POME concentration increased.

Table 1
Initial and final concentration of colour in POME

POME ratio (%)	Initial concentration (PtCo)	Final concentration (PtCo)
15	430	245
20	688	549
40	1244	1093
60	2454	2201

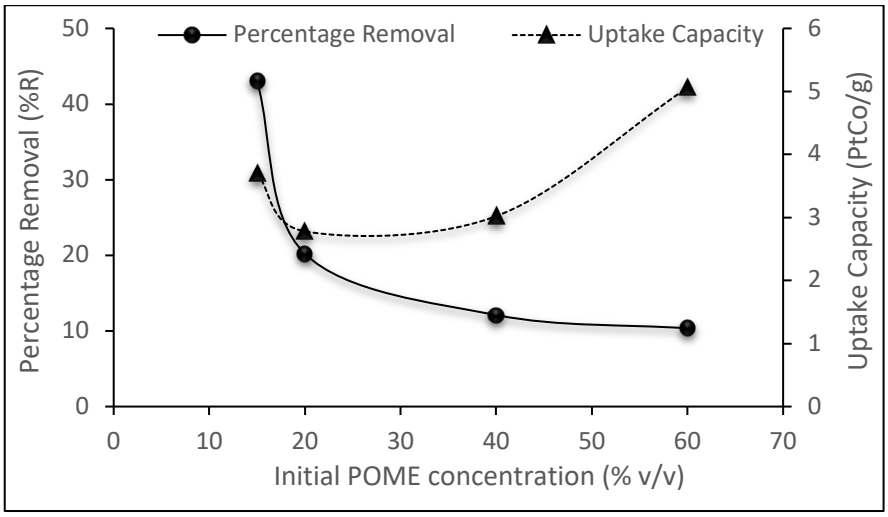


Fig. 1. Effect of initial POME concentration (expressed as dilution percentage, v/v) on colour removal. Conditions: 5.0 g adsorbent dosage, 60 minutes contact time and pH 4.8

This inverse relationship can be attributed to the saturation of available adsorption sites on the adsorbent surface. At lower initial concentrations, the number of colour molecules is relatively small compared to the available active sites, allowing for higher removal efficiency. However, as the initial concentration increases, the number of colour molecules exceeds the available adsorption sites, resulting in a lower percentage of removal. Despite this, the higher concentration gradient between the solution and the adsorbent surface at elevated initial concentrations enhances the mass transfer rate, thereby increasing the total amount of colour adsorbed [23]. These findings are in agreement with previous studies [23,25,31,32,33]. This confirms that initial POME concentration is a critical factor influencing the colour removal capacity of dolomite.

3.1.2 Effect of adsorbent dosage

Figure 2 illustrates the effect of adsorbent dosage (2.5 to 12.0 g) on the percentage removal of colour and the corresponding uptake capacity of thermally processed dolomite. The experiment was conducted under fixed conditions of 15% (v/v) initial POME concentration, 60 minutes contact time and pH 4.8. As shown, increasing the dosage from 2.5 g to 5.0 g led to a notable improvement in colour removal, with the maximum percentage removal of 47.78% and the maximum uptake capacity of 4.52 PtCo/g achieved at 5.0 g. Beyond this point, further increases in dosage resulted in a slight decline in removal efficiency. A similar trend was observed for uptake capacity, which rose sharply up to 5.0 g but declined slightly at higher dosages.

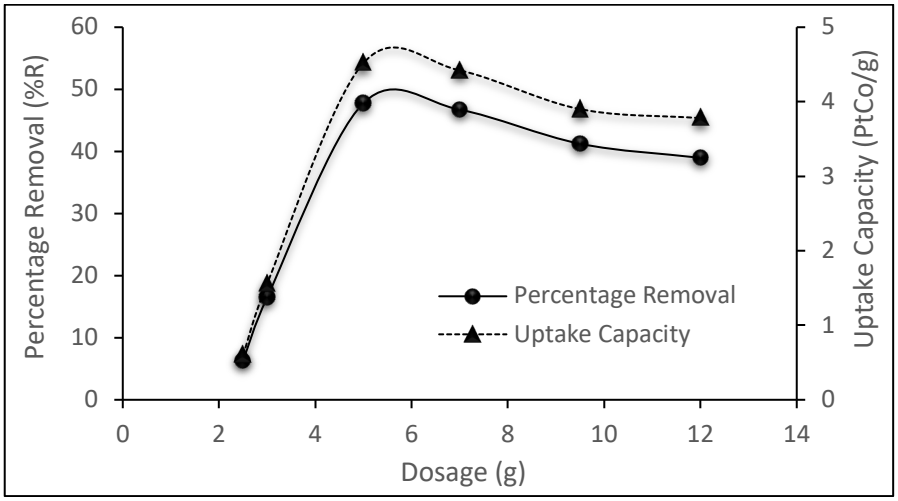


Fig. 2. Effect of adsorbent dosage on colour removal. Conditions: 15% (v/v) concentration, 60 minutes contact time and pH 4.8

The increase in percentage removal with rising adsorbent dosage (up to 5.0 g) can be attributed to the greater availability of active binding sites and increased adsorbent surface areas, enhancing interaction with colour molecules in the POME [34-35]. Also, thermally treated dolomite which is primarily composed of calcium magnesium carbonate, has a porous structure and large surface area that make it suitable for adsorbing any compounds from POME [36]. Heating the dolomite at 800 °C enhanced its surface characteristics by increasing porosity and surface area, which improved its ability to adsorb colour [20]. This thermal activation also promoted the formation of active compounds like calcium oxide (CaO) and magnesium oxide (MgO) on the surface, contributing to better adsorption through ion exchange and surface interactions with colour molecules [21]. This behaviour is consistent with findings reported in previous studies on POME and dye wastewater treatment, where increasing adsorbent dosage initially improves removal due to more accessible

binding sites [32,33,34,37,38]. However, beyond the optimum dosage, the removal percentage begins to plateau or decline slightly due to particle agglomeration or overlapping of adsorption site, which reduces the effective surface area accessible for adsorption [3,35,39]. Overcrowding of adsorbent particles may lower adsorption capacity per unit mass due to reduced mass transfer and under-utilization of sites. The decline in uptake capacity at higher dosages further confirms this behaviour, as the amount of colourant available per gram of dolomite becomes limited. According to Djelloul *et al.,* [40] this phenomenon may also be attributed to the unsaturation of adsorbent sites during the adsorption process. Thus, these results suggest that 5.0 g is the optimum dosage for efficient and cost-effective colour removal using thermally processed dolomite under the given experimental conditions.

3.1.3 Effect of contact time

Figure 3 shows the effect of contact time (15 to 240 minutes) on the percentage removal of colour and the corresponding uptake capacity using thermally processed dolomite. Under fixed conditions of 15% (v/v) initial POME concentration, 5.0 g adsorbent dosage and pH 4.8, both the percentage removal and uptake capacity increased rapidly within the first 60 minutes, followed by a slower rise up to 240 minutes. The maximum colour removal achieved 71.31% and the highest uptake capacity reached 6.66 PtCo/g at 180 minutes. Beyond this point, only minimal changes were detected up to 240 minutes, suggesting that equilibrium was nearly achieved.

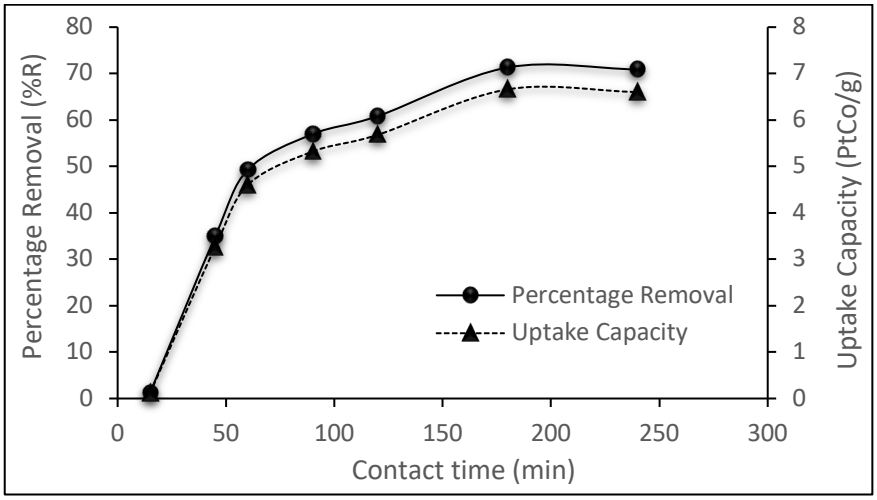


Fig. 3. Effect of contact time on colour removal. Conditions: 15% (v/v) concentration, 5.0 g adsorbent dosage and pH 4.8

The rapid adsorption at initial stage of the interaction time can be attributed to the abundance of available active binding sites on the dolomite surface and a high concentration gradient between the solution and the adsorbent [39-40]. As time progressed, the number of unoccupied binding sites decreased, and diffusion into internal pores became the rate-limiting step, slowing the adsorption process. This behaviour corresponds with earlier studies that describe a two-stage adsorption mechanism, a fast external surface interaction followed by a slower intraparticle diffusion process [3,32,34,41,42,43]. Saleh *et al*., [24] further explained that extending contact time beyond equilibrium does not significantly improve adsorption, as most active sites are already saturated. Thus, the observed plateau between 180 and 240 minutes indicates that equilibrium had been reached, making longer durations less practical for efficient batch operations. These findings confirm

that a contact time of 180 minutes is sufficient for achieving near-maximum colour removal from POME using thermally processed dolomite.

3.1.4 Effect of pH

Figure 4 shows the influence of pH (range 4 - 10) on the percentage removal of colour and the uptake capacity during adsorption using thermally processed dolomite. The experiment was conducted under fixed conditions of 15% (v/v) initial POME concentration, 5.0 g adsorbent dosage and 180 minutes contact time. The results show that both colour removal and uptake capacity improved with increasing pH from 4 to 7.5, with the maximum percentage removal of 79.91% and the highest uptake capacity of 7.4 PtCo/g observed at pH 7.5. Beyond this point, a slight decline in both values was observed as the pH increased to pH 10.

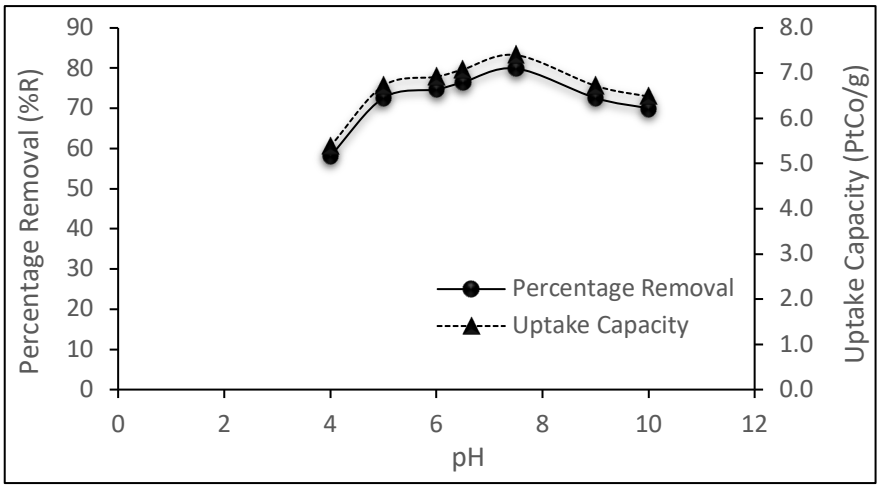
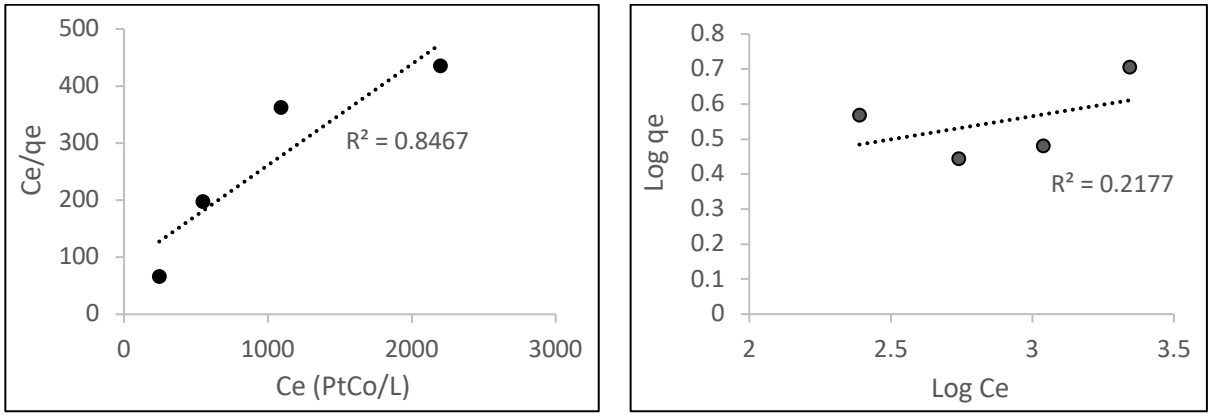


Fig. 4. Effect of pH on colour removal. Conditions: 15% (v/v) concentration, 5.0 g adsorbent dosage and 180 minutes contact time

The improvement in adsorption performance from acidic to neutral pH is attributed to the surface charge interactions between dolomite and the colour compounds in POME [32]. At low pH values, the high concentration of H^+ ions likely competes with the colour molecules for active adsorption sites, reducing removal efficiency [37]. As the pH increases, electrostatic repulsion decreases and more colour molecules can interact with the negatively charged dolomite surface, enhancing adsorption. However, at alkaline conditions (pH > 9), the removal slightly decreases, possibly due to the formation of negatively charged functional groups on both adsorbent and adsorbate, leading to repulsive interactions and reduced adsorption capacity [20]. Additionally, thermally treated dolomite contains CaO and MgO, which are sensitive to pH and may undergo partial dissolution or transformation at extreme pH levels (very high or very low), slightly altering the surface chemistry. This pattern is consistent with previous findings for colour removal from POME by other adsorbent, such as coal bottom ash [24], where pH strongly influenced adsorption by affecting both the adsorbent surface properties and ionization state of the pollutants. These results indicate that a near neutral pH 7.5 is optimal for achieving maximum colour removal from POME using thermally processed dolomite.

3.2 Evaluation of Adsorption Models
3.2.1 Isotherm models

The equilibrium data for colour removal from POME using thermally processed dolomite were assessed using the Langmuir and Freundlich isotherm models. The corresponding linear plots are presented in Figure 5, which illustrates the fitting of the data to both models. Table 2 presents the corresponding isotherm constant parameters for each model. The Langmuir isotherm analysis yielded a moderate fit, with a coefficient of determination (R^2) of 0.8467. The maximum adsorption capacity, q_{max} was determined to be 5.65 PtCo/g and the Langmuir constant, b was 0.0021 L/PtCo. The results suggest that the adsorption process likely involved monolayer coverage on a relatively homogeneous surface of the thermally processed dolomite. In contrast, the Freundlich model exhibited a poor correlation with a coefficient of determination (R^2) of 0.2177, indicating that the adsorption process did not conform well to heterogeneous multilayer adsorption. However, the Freundlich constant, n was 7.56 (1/n < 1), which still suggests favourable adsorption [44], although the overall fit was weak. This discrepancy implies that while some surface heterogeneity may exist, the adsorption behaviour is better described by the Langmuir model under the tested conditions. The finding is consistent with other adsorbents for colour removal from POME, such as palm kernel shells and empty fruit bunches [32], oil palm kernel shells [34], montmorillonite [38] and granular activated carbon [43], which also better fit with the Langmuir model compared to the Freundlich model.



(a) (b)

Fig. 5. Evaluation of colour removal using isotherm models (a) Langmuir (b) Freundlich

Table 2
Adsorption isotherm constant parameters for colour removal

Langmuir isotherm			Freundlich isotherm		
q_{max} (PtCo/g)	b (L/PtCo)	R^2	K_f (PtCo/g)(L/PtCo)$^{1/n}$	n	R^2
5.65	0.0021	0.8467	1.4733	7.56	0.2177

3.2.2 Kinetic models

The adsorption kinetics of colour removal from POME using thermally processed dolomite were analysed by applying three kinetic models, namely pseudo-first-order, pseudo-second-order and intraparticle diffusion. Linearized forms of these models were used to interpret the experimental data, as illustrated in Figure 6. Table 3 presents the corresponding kinetic constant parameters for

each model. The pseudo-first-order model yielded a moderate fit, with a coefficient of determination, R^2 of 0.8236 and a rate constant, K_1 of 0.017 min^{-1}. However, the pseudo-second-order model provided a stronger correlation to the data with a coefficient of determination, R^2 of 0.9844 and a rate constant, K_2 of 0.0021 g/PtCo.min. This indicates that the adsorption was likely governed by chemisorption, involving electron exchange or sharing between the adsorbent and the adsorbate [3]. The intraparticle diffusion model exhibited multilinear plot, suggesting that adsorption proceeded in multiple stages. The non-zero intercept indicates that boundary layer (film) diffusion also plays a role and intraparticle diffusion is not the sole rate-controlling step [44]. The finding is consistent with other adsorbents for colour removal from POME, such as banana peel [3], coconut shell activated carbon [23], coal bottom ash [24] and fly ash [45], which also better fit to the pseudo-second-order kinetic model than other models.

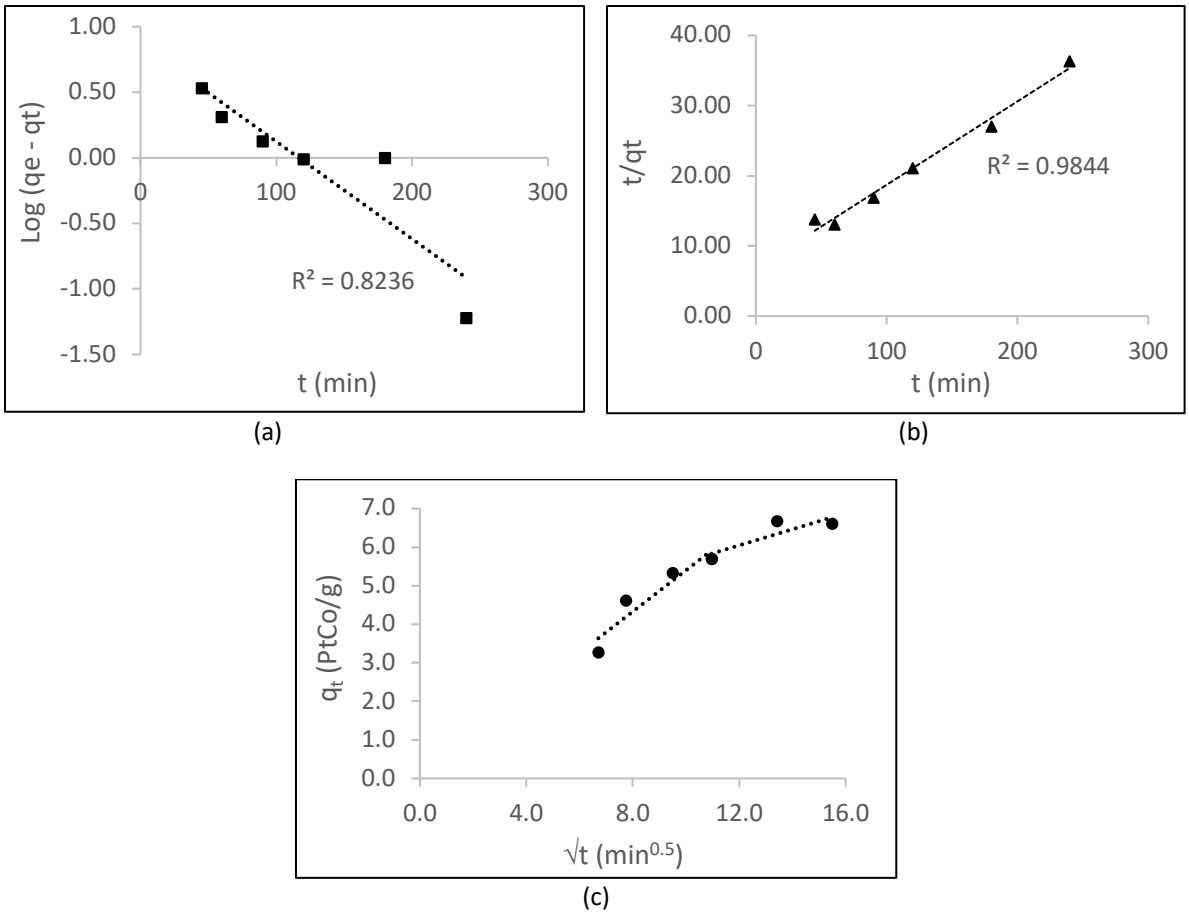


Fig. 6. Evaluation of colour removal using kinetic models (a) pseudo-first-order (b) pseudo-second-order (c) intraparticle diffusion

Table 3
Kinetic constant parameters for colour removal

Kinetic model	Parameters		
Pseudo-first-order	q_e (PtCo/g)	K_1 (min^{-1})	R^2
	7.35	0.017	0.8236
Pseudo-second-order	q_e (PtCo/g)	K_2 (g/PtCo.min)	R^2
	8.41	0.0021	0.9844
Intraparticle diffusion	K_{id} (PtCo/g.$min^{0.5}$)	C	R^2
	0.5351	0.0471	0.8835
	0.2088	3.5394	0.7452

4. Conclusions

This study demonstrated that thermally processed dolomite is an efficient material for treating colour from POME. The batch adsorption experiments showed that factors such as initial concentration, adsorbent dosage, contact time and pH significantly influenced removal efficiency and uptake capacity. The optimum conditions for maximum colour removal of 79.91% and maximum uptake capacity of 7.4 PtCo/g were achieved at 15% (v/v) initial POME concentration, 5.0 g dolomite dosage, 180 minutes contact time and pH 7.5. These findings confirm the adsorbent's suitability under practical operating ranges. The adsorption mechanism was investigated using both isotherm and kinetic models. The equilibrium results aligned best with the Langmuir isotherm (R^2 of 0.8467), suggesting that adsorption occurred as a monolayer on a relatively uniform surface. Kinetic analysis revealed that the pseudo-second-order model showed the highest correlation (R^2 of 0.9844), suggesting that chemisorption was the key mechanism driving the process. These outcomes validate the potential of thermally processed dolomite as a sustainable material for treating coloured wastewater and lay the groundwork for scaling dolomite-based treatment systems in palm oil mill effluent applications. However, this study was limited to batch mode experiments under controlled laboratory conditions. Further research is recommended to evaluate the adsorbent's regeneration potential, long-term stability, and efficiency under continuous flow systems. Pilot-scale studies and economic assessments should also be conducted to confirm feasibility for industrial implementation.

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