

Adsorption of pollutants from palm oil mill effluent using natural adsorbents: optimization and isotherm studies

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ABSTRACT

Batch adsorption of COD and NH₃-N from palm oil mill effluent onto natural adsorbents from activated coconut shells carbon (ACSC), activated cow bones powder (ACBP) and zeolite has been investigated under hydrophobic and hydrophilic conditions. The study also investigates the suitability of the natural adsorbents for the preparation of composite. The result of the investigation revealed that reduction of COD and NH₃-N was optimum under hydrophobic condition at ratio (15:25) volumetric dosage of ACSC:ACBP, respectively. This was achieved at 79.8% reduction of COD and 48.2% removal of NH₃-N. Similarly, under hydrophilic condition, the reduction of COD and NH₃-N was optimum at 35 cm³ at 45.2% reduction of COD and 65.4% removal of NH₃-N. Further optimization study under hydrophobic-hydrophilic conditions revealed that the optimum reduction of pollutants was observed at 25:15 cm³ volumetric dosage which was equivalent to 78.2% reduction of COD and 68.5% removal of NH₃-N. The composite was prepared at 80:20 adsorbent:binder ratio which was the optimum ratio achieved for the reduction of the investigated parameters under batch study. Equilibrium data fitted better to the Langmuir isotherm for both reductions of COD and NH₃-N which indicates that homogeneous adsorption occurred on a monolayer surface. The result of the kinetic uptake reveals that kinetic data fitted better to the pseudo-second order model which suggested that adsorption was by chemisorption. The intraparticle diffusion model indicates that adsorption was not only affected by rate controlling step but also influenced by adsorption along the boundaries.

Keywords: Palm oil mill effluent; Composite; Adsorption equilibrium; Kinetics; Response surface methodology

1. Introduction

The high production of effluent from palm oil mill has increased research methods in order to minimize the effect of pollution on the receiving waters as a result of discharge.

High cost of treatment or insufficient technical expertise are the two major factors that are attributed to water pollution in most of the developing countries in the world [1]. The discharge of effluent without proper treatment affects the environment significantly due to high concentration of organic pollutants which are toxic to the aquatic environment thereby affecting the health of the flora and fauna [2–4]. Therefore, a cost-effective treatment of high strength

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industrial wastewater such as palm oil mill effluent (POME) has become a major concern to mill operators to avoid violating stringent regulations regarding discharge standards as stipulated by the ministry of environment [5,6].

In the palm oil industry, the most conventional treatment method is biological process of effluent management towards safe discharge such as the use of anaerobic digestion [7,8], aerobic treatment system such as advanced oxidation including photocatalysis and Fenton oxidation [9], membrane separation [10] and solvent extraction [11]. However, the conventional approach especially the application of biological treatment system is very expensive and in most of the cases, they are not effective for the treatment of organic pollutants of high strength wastewater at low concentration. Among the wastewater treatment methods, adsorption is more applicable because of its high potential to treat pollutants at low concentration which is considered as the major limitation of existing conventional treatment methods. In addition, the cost of treatment is considered economical since the adsorbents are abundant in nature.

Adsorption is also considered as a green technology because of the potential of recyclability of the adsorbents and the production of quality-treated effluent suitable for discharge. Low-cost adsorbents such as peat [12], *Moringa* [13], bones [14], banana peel [15], coconut shells [16], wood [17], zeolite [18] have been reported in the literature for the reduction of pollutants from POME. The application of copper-modified scoria powder and the use of pumice have been reported for the removal of organic compounds [19–21]. However, classification of adsorbent for the synthesis of composite for the adsorption of pollutants on the basis of their behaviour in aqueous solution has rarely been reported in the research phase. The choice of adsorbent is determined by its ability to reduce the priority pollutant in wastewater. Adsorbents that readily adsorb non-polar solutes are hydrophobic in nature while polar solutes are readily adsorbed on hydrophilic surface [22].

The characteristics of adsorbent are determined by the angle between the liquid drops in contact with the interface between the adsorbent and adsorbate. Hydrophobic adsorbents have contact angle greater than 90° while surface that readily dissolves in aqueous solution for the adsorption of pollutants are known to have contact angle less than 90° [23]. Activated coconut shell and activated cow bone powder are hydrophobic because of the inclination of the surface when in aqueous solution at angle greater than 90° [23]. Activated cow bone powder has the ability to adsorb pollutants in wastewater based on the hydroxyapatite characteristics which is a predominant chemical composition [24]. In addition, cow bones contain both carbon and mineral composition which makes the adsorbent possess a very promising treatment agent of organic pollutants in wastewater. Activated coconut shell is hydrophobic on the basis of the composition of the lignocellulosic characteristics [25]. Furthermore, zeolite is known to be hydrophilic in nature and has been reported to be a very effective adsorbent for the reduction of ammonia-nitrogen in wastewater [26]. In the present work, natural adsorbents of coconut shells, cow bones and zeolite were synthesized and prepared as composites for the reduction of organic and inorganic pollutants of POME. The main objective of this work was to investigate the potential of the adsorbents under

different conditions for the reduction of COD and $\text{NH}_3\text{-N}$ from POME.

2. Methods and materials

2.1. Adsorbents

In this study, coconut shells were obtained at Klan Hoe Plantation, Johor, Malaysia. The samples were washed and dried for 24 h under sunlight. The dried coconut shells were heated up to a carbonization temperature of 500°C for 2 h at $10^\circ\text{C}/\text{min}$. After the pyrolysis of the chars, the activated coconut shells were washed and oven dried for 24 h at 105°C . After then, the dried samples were mixed with 450 mL sulphuric acid and were allowed to dry for 24 h [15]. The activated coconut shell was ground to working particle size of $150\ \mu\text{m}$. Cow bones used for the study were obtained from fresh meat market located in Parit Raja district of Johor, Malaysia. The bones were thoroughly washed before drying and pyrolysis at 700°C for 5 h [14]. The activated cow bone char were washed and oven dried for 24 h at 105°C . After then, the dried samples were reduced to working particle size of $150\ \mu\text{m}$ using the roller grinder. Zeolite (clinoptilolite) used for the study was supplied in a wrapped polythene bag by PT Zeolita Jakarta, Indonesia. The samples were washed and oven dried at 120°C for 18 h [27]. The three adsorbents were stored in different airtight plastic containers with proper labels. The classification of the materials as hydrophobic and hydrophilic adsorbent was based on pendant drop contact angle test [28]. The efficiency of the adsorbents was investigated for the reduction of COD and $\text{NH}_3\text{-N}$ from POME. The optimum condition obtained from the batch study was used to determine the ratio of the adsorbents used for the preparation of the composite. The adsorbent materials were of different densities, therefore the volume by weight of the dosage occupied in the POME was determined from the bulk densities of the particle sizes of the adsorbents according to ASTM 2854, Latiff et al. [14]. The optimum condition of the hydrophobic-hydrophilic ratio was used to determine the optimum condition by percentage of the starting materials that was mixed with the ordinary Portland cement (OPC) for the preparation of the composite. The optimum ratio of the adsorbent of each of the starting materials was mixed with the optimum dose of OPC. The materials were mixed homogeneously using mechanical stirrer. Measured sample of distilled water by adsorbent weight was added to the mixture and were thoroughly mixed together until paste was formed. The paste was allowed to harden after 3 d. The curing process was undertaken to improve on the strength of the composite after which the adsorbent was oven dried at 104°C for 24 h. Prior to the investigation, the particles sizes were washed with distilled water and dried for 24 h in order to remove trapped impurities and external materials on the surface of the adsorbent which may affect the outcome of the investigation.

2.2. Characterization of adsorbents

The specific surface area of the composite adsorbent was determined using ASAP 2020 using the Brunauer-Emmett-Teller (BET) method. The samples were irradiated using the

Fourier transform infrared spectroscopy (FT-IR) to determine the active available functional groups on the surface of the adsorbent. Characterization of the adsorbent was carried out before and after adsorption.

2.3. Sampling of POME

POME was collected aseptically from PPNJ Kilang Sawit, Kluang Johor. The samples were put in a 10-L plastic container, transported and stored according to the standard method of transportation, storage and preservation of water and wastewater by the American Public Health Association (APHA) [29]. Prior to storage, the initial concentration pump was used for the filtration of suspended solids (SS) while the *n*-hexane extraction method was used to determine the initial concentrations of oil and grease (O&G) although the residual concentration of the priority parameters of COD and NH₃-N was used for the investigation of the efficiency of the adsorbents.

2.4. Batch adsorption study

Equilibrium batch experiments were carried out in a 250-mL conical flasks containing 100 mL of POME. The experiments were conducted at room temperature using the orbital shaker at operational condition of 150 rpm shaking speed, 105 min contact time, 150 μm particle size at pH 7. The supernatant for each of the samples containing the adsorbents was filtered at the end of the experimental contact time and the efficiency of the adsorbents was investigated for the reduction of COD from the POME according to the standard closed reflux method 5220A. Similarly, the concentration of NH₃-N in the adsorbate was measured using the Nessler method (D1426-08). The experimental data obtained for all assays were conducted in triplicate and were recorded in percentage average. The reduction percentage of COD and NH₃-N from POME was calculated according to Eq. (1).

$$\% \text{ Removal} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where C_0 and C_e represent the initial and equilibrium concentrations of COD and NH₃-N in POME, respectively.

2.5. Adsorption isotherm studies

The equation of adsorption isotherm is defined by the expression (q_e vs. C_e) according to the nature of surface and shape. Two isotherm equations are investigated in this work. A description of monolayer coverage of adsorption of investigated parameter on a homogenous surface is evaluated according to the Langmuir equation. This is based on the hypothesis that adsorbed molecule has equal activation energy.

An expression to describe the linearized Langmuir equation is given by Eq. (2):

$$x = \frac{1}{q_{\text{mon}} b C_e} + \frac{1}{q_{\text{mon}}} \quad (2)$$

where C_e is the saturated amount of pollutants adsorption at equilibrium concentration (mg/L), q_{mon} is monolayer capacity of the adsorbent (mg/g), and b is the adsorption constant (L/mg). The slope and intercept describes the q_{mon} and K_L , respectively. The expression is used to describe the fitness of the experimental data to the Langmuir equation. The Langmuir isotherm can also be expressed as a dimensionless constant which is referred to as the separation coefficient. This can be illustrated in Eq. (3) as follows:

$$R_L = \frac{1}{1 + K_L C_0} \quad (3)$$

where C_0 is the initial concentration of pollutants (mg/L), used to describe the shape of the isotherm. R_L is defined as irreversible if ($R_L = 0$), favourable if ($0 < R_L < 1$), unfavourable if ($R_L > 1$) and linear if ($R_L = 1$) [23]. The concentration of solute in the adsorbate from trace to saturation can be described using the Freundlich isotherm equation. The model describes the distribution of adsorption sites and the energies that enhance the binding sites for adsorption. In Freundlich equation, a non-ideal adsorption on a heterogeneous surface was used to describe the reduction of COD and NH₃-N from POME. The Freundlich isotherm is illustrated in Eq. (4) as follows:

$$q_e = K_f C_e^{1/n} \quad (4)$$

A plot between $\ln q_e$ against $\ln C_e$ from the Freundlich isotherm is used to evaluate the surface heterogeneity of the adsorbent. The values of n and K_f are calculated from the slope and intercept of the linear plot. The coefficient of K_f is used to describe the adsorption capacity while n describes the adsorption intensity which indicates favourability of investigated parameters in POME. When the coefficient of $1/n < 1$, adsorption is favourable and unfavourable when $1/n > 1$.

2.6. Adsorption kinetics study

The adsorption of pollutant parameters on the surface of the adsorbent is time related. The rate of diffusion within the pores of the adsorbent and towards the external surface determines the rate of adsorption. In order to determine the rate of adsorption as a result of the diffusion process and mass transfer within the adsorbent and the external surface, experimental data are fitted to kinetic models to describe the pattern of adsorption. Two kinetic models were used to fit experimental data in this study which are the pseudo-first order and the pseudo-second order kinetic models.

The Lagergren kinetic equation popularly known as the pseudo-first order assumes that the rate of change of the uptake of solutes in the adsorbate is proportional to the difference between the saturation concentration and the amount of uptake of the pollutant parameter in the adsorbate. The equation is expressed as Eq. (5). The plot of $\ln(q_e - q_t)$ against t gives a slope of K_1 and intercept of $\ln q_e$. The pseudo-second order fits experimental data based on the adsorption capacity

in the solid phase. The pseudo-second order kinetic equation is represented by Eq. (6).

$$\frac{\delta q_t}{\delta t} = K_1(q_e - q_t) \tag{5}$$

$$\frac{\delta q_t}{\delta t} = K_2(q_e - q_t)^2 \tag{6}$$

where q_e and q_t are used to describe the amount of adsorption of COD and $\text{NH}_3\text{-N}$ achieved at equilibrium contact time (t). K_1 signifies rate constant of pseudo-first order (1/min), while K_2 is the rate constant of pseudo-second order adsorption.

3. Results and discussions

3.1. Selection of particle size

The batch adsorption study was conducted to investigate the efficiency of activated coconut shells carbon (ACSC), activated cow bone powder (ACBP) and zeolite under hydrophobic and hydrophilic conditions. Prior to the analysis, sampling of POME was obtained three times ($N = 3$), the initial concentration of the physico-chemical parameters was observed as COD $57,500 \pm 2.16$ mg/L, $\text{NH}_3\text{-N}$ 425 ± 1.24 mg/L, SS $1,520 \pm 2.9$ mg/L, oil and grease (O&G) $1,622 \pm 2.1$ mg/L. Experimental data were achieved at the condition of shaking speed 150 rpm, contact time 105 min, pH 7 at 25°C. The results of the supernatant were obtained at equilibrium concentration at different dosage of adsorbents. The study was conducted using four particle sizes (75, 150, 250 and 300 μm) for the ACSC, ACBP and zeolite at 25 cm³ by volume of adsorbent dosage which was obtained from the bulk densities in Table 1.

Adsorbents used in the phase of the study were classified on the basis of their hydrophobic and hydrophilic characteristics according to the behaviour of the surface in contact with water. From the previous study, activated carbon of coconut shell and cow bone powder was classified as hydrophobic adsorbents while the zeolite was classified as the hydrophilic adsorbent [23]. The result obtained for the particle size selection of the adsorbent materials indicated that ACBP achieved optimum removal efficiency for both COD and $\text{NH}_3\text{-N}$ at 71.1% and 42.2%, respectively, using 150 μm particle size. Even though there was no significant difference in the efficiency of the adsorbents for the reduction of COD except with zeolite. Findings revealed that ACSC achieved better removal efficiency for COD more than ACBP and zeolite. The removal efficiency of the adsorbent for the reduction of COD

was observed to be 79.24% using 75 μm sieve size while least removal efficiency (78.16%) was achieved at 300 μm particle size. There was optimum removal efficiency of $\text{NH}_3\text{-N}$ using the 150 μm particle size. Results indicated that reduction of $\text{NH}_3\text{-N}$ was optimum using zeolite compared with ACSC and ACBP. The results obtained for the batch adsorption of COD and $\text{NH}_3\text{-N}$ from POME are presented in Figs. 1a and b, respectively.

3.2. Batch adsorption study on hydrophobic and hydrophilic adsorbents

From the result obtained for the starting materials, it was observed that the particle sizes of 150 μm achieved better reduction of COD and $\text{NH}_3\text{-N}$ compared with other particle sizes. This particle size considered as the most effective particle size of the materials selected even though there were few cases of other particle sizes achieving better removal efficiencies. Therefore, the 150 μm size single adsorbents were adopted for the batch studies carried out for the investigation of the possible effect of mixed adsorbents on the reduction of COD and $\text{NH}_3\text{-N}$ from POME. The result of the batch study for the adsorbents that possessed hydrophobic characteristics is

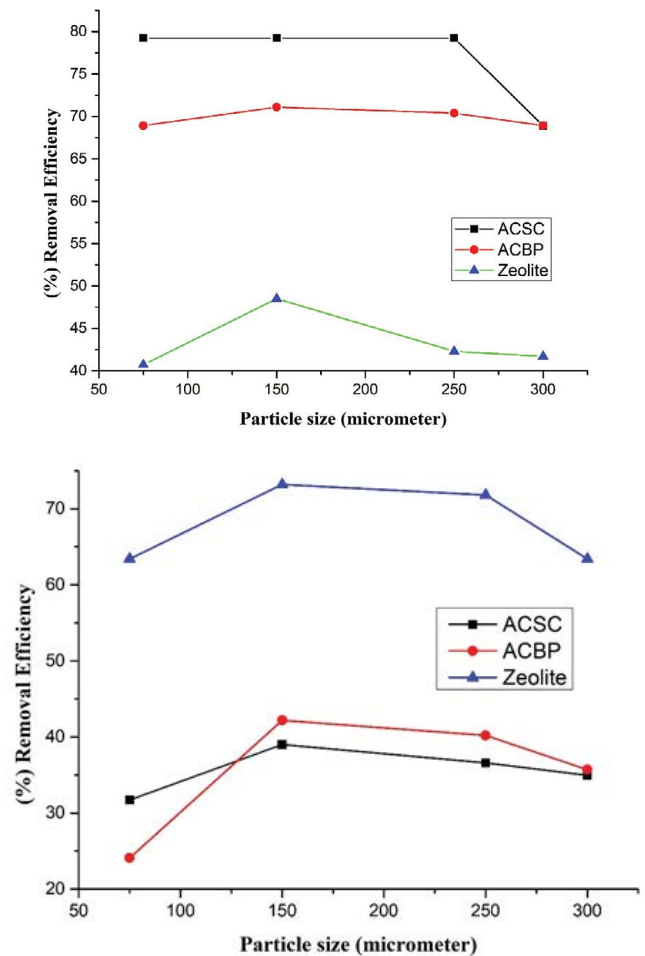


Fig. 1. (a) Batch adsorption of COD. (b) Batch adsorption of $\text{NH}_3\text{-N}$.

Table 1 Bulk densities of adsorbents

Particle size (μm)	Activated cow bone powder	Activated coconut shell carbon	Zeolite
75	0.49	0.470	0.810
150	0.63	0.570	0.970
250	0.88	0.624	0.987
300	0.98	0.640	1.020

illustrated in Fig. 2a while the effect of hydrophilic behaviour for the reduction of investigated parameters is presented in Fig. 2b. The optimal reduction of COD and $\text{NH}_3\text{-N}$ in Fig. 2a was observed in the ratio 15:25 of ACBP:ACSC. On the other hand, the optimal reductions of COD and $\text{NH}_3\text{-N}$ were observed at 35 cm^3 , respectively, by volume of dosage of zeolite applied (Fig. 2b).

3.3. Batch adsorption study on hydrophobic–hydrophilic adsorbents

The combined effect of the hydrophobic and hydrophilic characteristics of adsorbents for the reduction of COD and $\text{NH}_3\text{-N}$ is presented in Fig. 3.

The reduction efficiency for COD was high at all operational conditions except at 0:40 of the hydrophobic–hydrophilic ratio and the optimum reduction of parameters was observed at 25:15 by volume of the applied dosage. It was observed that the reduction of $\text{NH}_3\text{-N}$ increases as the hydrophilic ratio decreases until when optimum reduction was achieved at the ratio equivalent to the optimum reduction achieved for COD. From the findings, it was revealed that

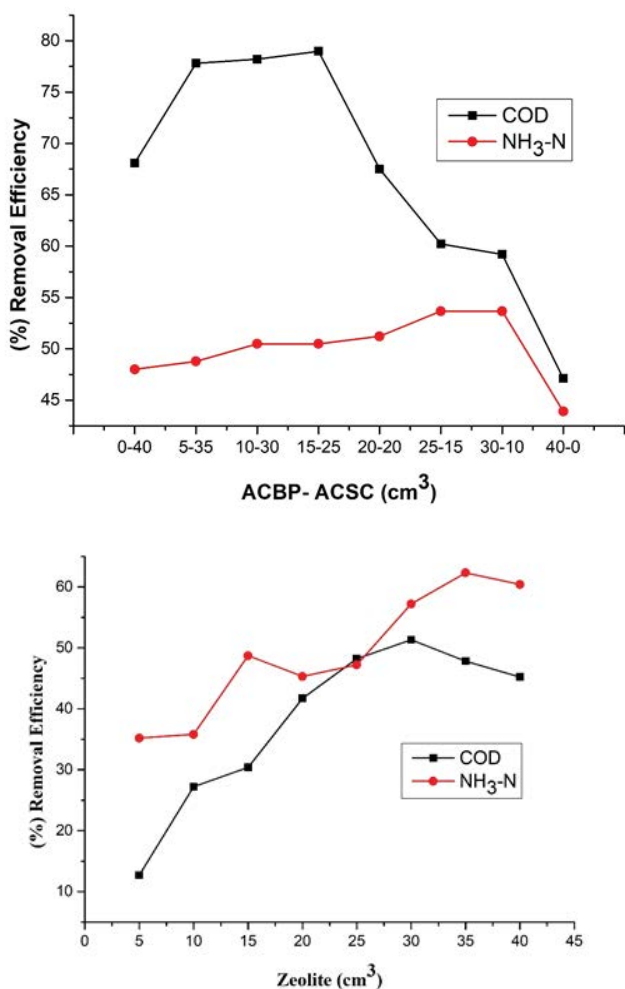


Fig. 2. (a) Optimization of hydrophobic adsorbent. (b) Optimization of hydrophilic adsorbents.

the reduction of COD and $\text{NH}_3\text{-N}$ from POME on hydrophobic–hydrophilic adsorbents was achieved optimally at 25:15, respectively, dosage by volume.

3.4. Batch adsorption study on adsorbent–binder

The effect of adsorbent–binder ratio to determine the optimum condition for the combination of hydrophobic and hydrophilic adsorbents from the optimum conditions from Fig. 3 was used to estimate the amount of adsorbent utilized in Fig. 4. The required adsorbent ratio in Fig. 4 was evaluated from the relationship between the bulk density of the adsorbent and the adsorbent dosage applied and recorded at the optimum reduction of COD and $\text{NH}_3\text{-N}$ that was achieved using the least dosage of binder. After which the adsorbents were combined with binder to produce a composite (Fig. 4). In this study, the ordinary Portland cement (OPC) was used as the binder. The result obtained from the removal efficiency of the adsorbent–binder application revealed that there was no reduction in the efficiency of the composite as a result of the effect of the binder. It was observed that at minimum ratio of OPC applied, higher reduction of COD and $\text{NH}_3\text{-N}$ was achieved. The amount of the dosage of the adsorbent by volume of the single adsorbents used for the preparation of a composite is presented in Table 2. Batch study was conducted at 40 cm^3 volumetric dosage and was investigated for the reduction of COD and $\text{NH}_3\text{-N}$ from POME. The result of the removal efficiency of the composite is shown in Fig. 4.

The percentage by weight of the adsorbent dosage applied was estimated in terms of the optimum ratio obtained at the least application of binder. The optimum condition for the reduction of COD and $\text{NH}_3\text{-N}$ was obtained at adsorbent–binder ratio which is equivalent to 80:20.

3.5. Surface area of composite

The Brunauer–Emmett–Teller (BET) surface area of the prepared composite was investigated from the analysis of the N_2 adsorption isotherm using sample density of 1 g/cm^3 within equilibrium interval of 5 s at a temperature of

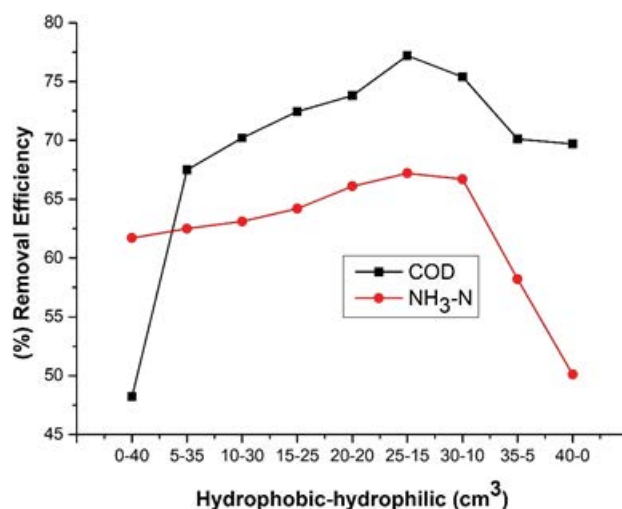


Fig. 3. Hydrophobic–hydrophilic behaviour of adsorbents.

77.31 K. The values of the isotherm plotted were evaluated. It was observed that the BET surface area of the composite was 248.3987 m²/g, the pore volume was 0.16564 m³/g while the pore size was 26.6732 Å which is equivalent to 2.667 nm. It was revealed that most of the pore size were mesoporous (20–500 Å). Based on IUPAC classification, a material is microporous if the pore size is <20 Å and macroporous when it is >500 Å and mesoporous if the range of particle size is between 20 and 500 Å [29].

3.6. Surface functional groups

The active functional groups available on the surface of adsorbents were determined using the FT-IR spectra. The bands were obtained to determine the bonding and cross-linkage on the surface of the composite before and after adsorption (Fig. 5).

The band 3,200 was attributed to OH Stretching vibration, the band 1,657 was assigned to C=O vibration. The band

at 1,051 was attributed to C–OH. Meanwhile the bands 982.04, 873.64 and 711.18 signified CH out-of-plane vibrations in substituted ethylenic systems. The band 1,628 cm⁻¹ was observed before and after adsorption which indicated the significance of C=C stretching vibration before and after the adsorption. In the spectra observed after adsorption, there was a shift in the spectra 1,051–1,030 cm⁻¹ which signifies the presence of stretching vibration of esters groups. A reduction in peak of the C–O–H stretching vibration was observed after adsorption. The effect of the hydroxyl, carbonyl and carboxylic group on the available active sites of the composite was responsible for the adsorption of the pollutants.

3.7. Adsorption isotherm

The application of empirical model for the prediction of experimental data is very significant for the interpretation of pattern of adsorption of pollutant parameters. In this

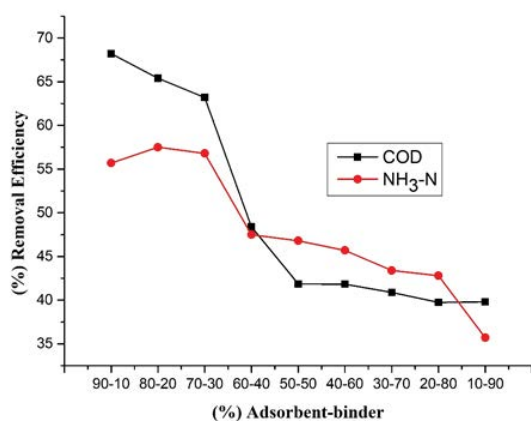


Fig. 4. Optimization of the adsorbent–binder ratio.

Table 2
Mixing ratio of adsorbents

Adsorbents	% Adsorbent									
	90	80	70	60	50	40	30	20	10	
	Weight of adsorbent (cm ³)									
ACBP	8.43	7.50	6.56	5.62	4.68	3.75	2.81	1.88	0.94	
ACSC	14.06	12.50	10.94	9.38	7.81	6.25	4.69	3.12	1.56	
Zeolite	13.50	12.00	10.50	9.00	7.50	6.00	4.50	3.00	1.50	
	% Binder									
	10	20	30	40	50	60	70	80	90	
	Weight of binder (cm ³)									
	4	8	12	16	20	24	28	32	36	
	% Removal efficiency of composite									
Organic pollutants (mg/L)										
COD	69.80	66.14	64.20	50.00	42.30	42.00	41.00	39.00	39.60	
NH ₃ -N	55.40	59.00	58.00	49.00	49.00	46.30	44.00	43.20	35.98	

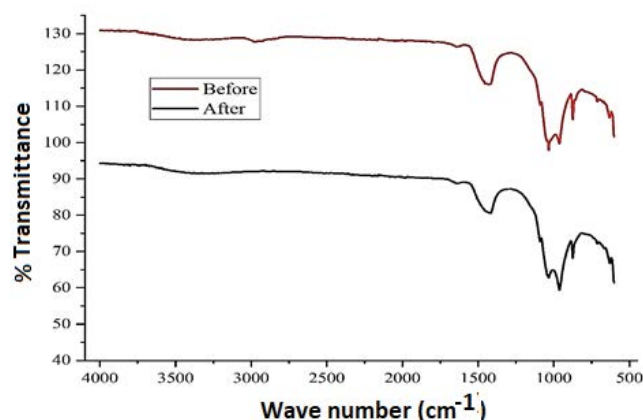


Fig. 5. Functional groups on composite before and after adsorption.

study, experimental data were fitted to the Langmuir and Freundlich isotherm equations to determine the nature of the adsorption of COD and $\text{NH}_3\text{-N}$ on the composite. A linearized plot to represent Langmuir isotherm equation for the reduction of COD and $\text{NH}_3\text{-N}$ is represented in Figs. 6a and b. Freundlich equation used to describe experimental data for the reduction of COD and $\text{NH}_3\text{-N}$ is illustrated in Figs. 6c and d. The coefficient of both isotherm models is represented in Table 3.

The results of the investigation revealed that experimental data fitted better to the Langmuir equation for the reduction of both COD and $\text{NH}_3\text{-N}$ from POME. A correlation coefficient (R^2) for the reduction of COD and $\text{NH}_3\text{-N}$ on the Langmuir isotherm was obtained as 0.994 vs. 0.986 for Freundlich isotherm. Similarly, experimental data fitted better to the Langmuir isotherm for the adsorption of $\text{NH}_3\text{-N}$ with an R^2 value of 0.9778 as against 0.968 was obtained for the experimental data fitted to the Freundlich isotherm.

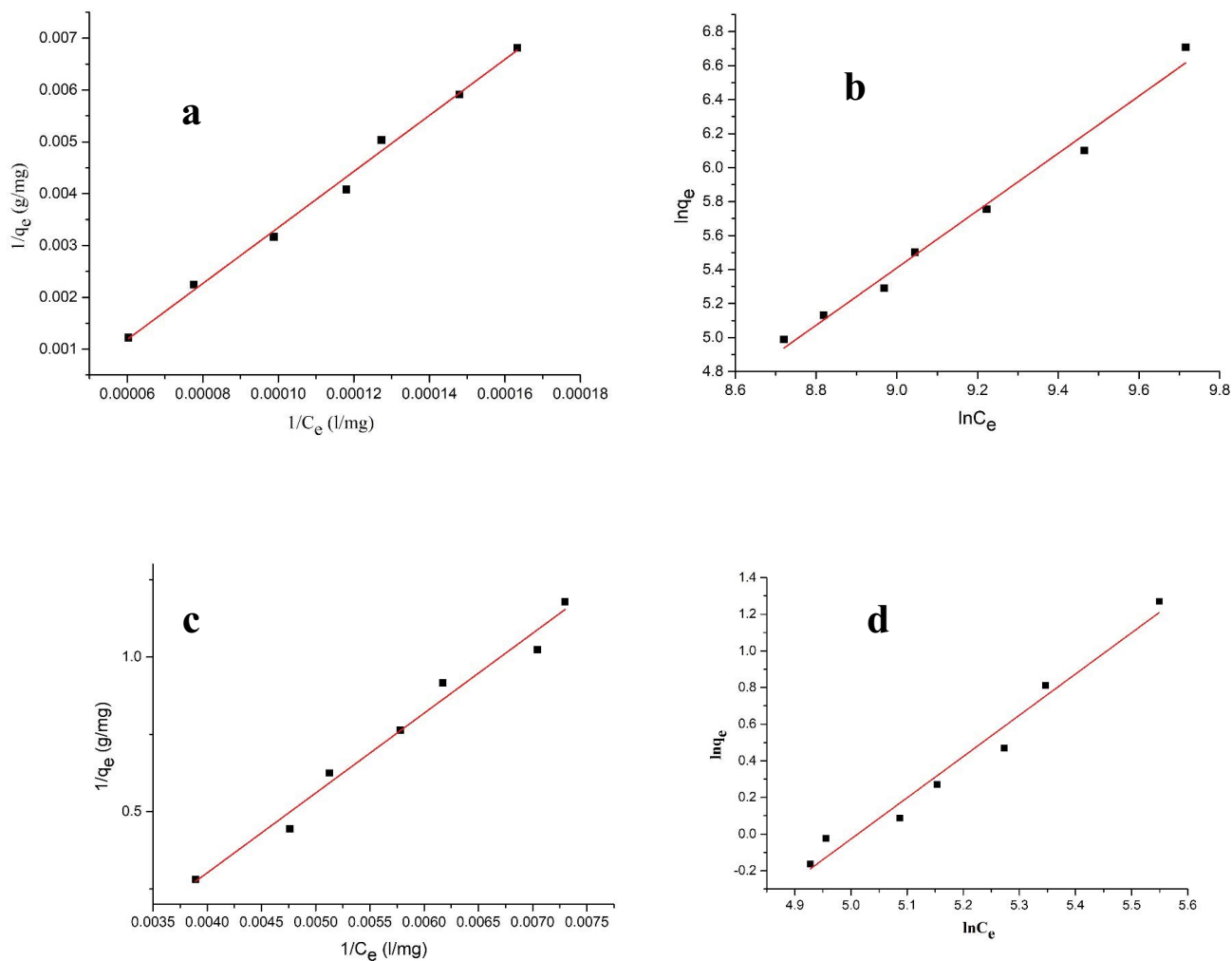


Fig. 6. Adsorption Isotherm on experimental data (operational conditions: 303 K, pH 7, 150 rpm, particle size 1 mm) (a) linearized Langmuir isotherm for COD reduction, (b) linearized Freundlich isotherm for COD reduction, (c) linearized Langmuir isotherm for adsorption of $\text{NH}_3\text{-N}$, (d) linearized Freundlich isotherm for adsorption of $\text{NH}_3\text{-N}$.

Table 3

Langmuir and Freundlich Isotherms constants for the reduction of COD and $\text{NH}_3\text{-N}$ from POME on composite

Parameter	Composite adsorbent						
	Langmuir isotherm				Freundlich isotherm		
	q_{\max} (mg/g)	k_L (l/mg)	R_L	R^2	K_F	n	R^2
COD	485.44	0.0038	0.3134	0.9935	0.00578	1.68548	0.9859
$\text{NH}_3\text{-N}$	38.70	0.9979	0.0024	0.9777	0.00126	2.25128	0.9680

This indicated that the adsorption sites and the energies of adsorption for the reduction of COD and adsorption of $\text{NH}_3\text{-N}$ from POME were homogeneously distributed on the surface of the composite. The favourability of the adsorption process was evaluated using the separator coefficient (R_L). A separator coefficient is determined by $0 < R_L < 1$. Adsorption is favourable if $R_L < 1$ and unfavourable if $R_L > 1$ [30,31]. The values of R_L evaluated for the reduction of COD was 0.3134 while 0.0024 was obtained for the adsorption of $\text{NH}_3\text{-N}$ from the analyte. This observable trend indicates favourable adsorption of COD and $\text{NH}_3\text{-N}$ from POME on the composite.

3.8. Adsorption kinetics

The rate of adsorption of COD and $\text{NH}_3\text{-N}$ from POME was investigated using two common adsorption kinetics model. The kinetic equations are the pseudo-first order and the pseudo-second order kinetic models. The linearized plot represents pseudo-first order using $\ln(q_e - q_t)$ vs. t while the pseudo-second order is defined by t/q_t vs. t . It was observed that the kinetics of adsorption of COD and $\text{NH}_3\text{-N}$ was defined by the higher R^2 of 0.987 against 0.990, respectively, compared with values obtained for the pseudo-first order model which was obtained as 0.931 and 0.936, respectively, for COD and $\text{NH}_3\text{-N}$ which indicates that the pseudo-second order model described better the pattern of adsorption. The result obtained for the kinetic constants for both pseudo-first and second order models for the reductions of COD and $\text{NH}_3\text{-N}$ from POME is presented in Table 4.

3.9. Adsorption mechanism

Controlling steps that determine the rate of adsorption can be influenced through mass transfer across the external boundary, the binding process at the internal and external surface of adsorbent, the diffusion of the adsorbate to the site of adsorption which is determined through pore diffusion either by the liquid pores or by solid surface mechanism [31–35]. A linearized plot for the adsorption of $\text{NH}_3\text{-N}$ and the reduction of COD from POME indicated that a linearized plot did not pass through the origin. This suggests that intraparticle diffusion is not the only rate governing mechanism. By implication, it can be deduced that the adsorption of $\text{NH}_3\text{-N}$ and COD also occurred through boundary layer diffusion. The acidic functional groups including the hydroxyl, carbonyl and carboxyl groups on the composite provide the available active sites for the adsorption process. The results of the intraparticle diffusion used to describe the mechanism

of adsorption of COD and $\text{NH}_3\text{-N}$ from POME on the composite is illustrated in Figs. 7a and b, respectively.

Two stages can be observed in the reduction of COD and adsorption of $\text{NH}_3\text{-N}$ from POME. There was no rate limiting step in the first stage because of rapid pore diffusion which influenced adsorption of the investigated pollutant parameters. The first stage was observed almost linear in the two cases (Figs. 7a and b) but did not have diffusion from the origin which implies that the adsorption was not only by rate limiting step. The mass transfer was observed in the second stage in Fig. 7a after q_e was observed at 303.989 mg/g before saturation occurred and in Fig. 7b, the mass transfer was observed below the linearized plot.

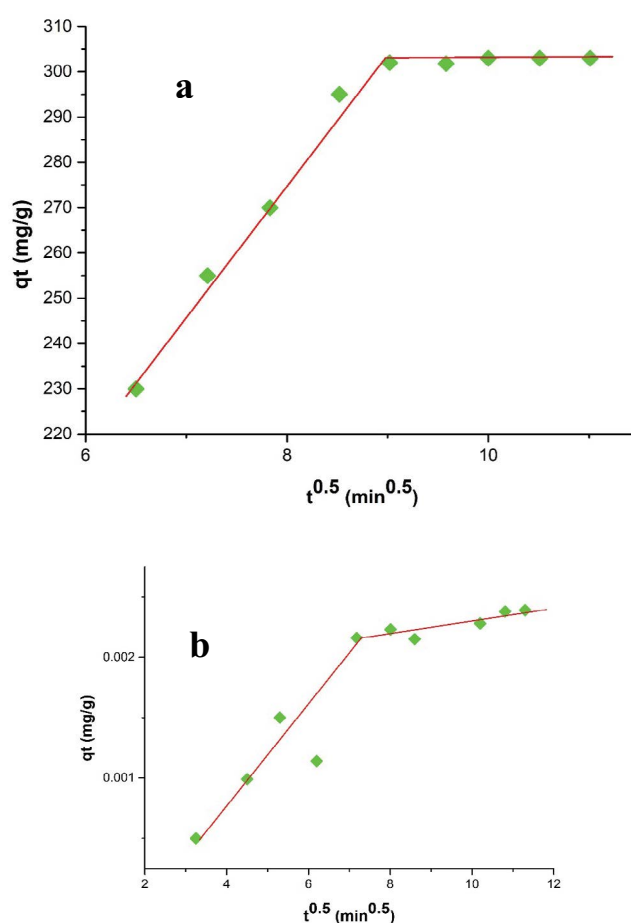


Fig. 7. Weber and Morris intraparticle diffusion graph (a) Reduction of COD, (b) adsorption of $\text{NH}_3\text{-N}$ on composite.

Table 4
Kinetic constants for the reduction of COD and $\text{NH}_3\text{-N}$ from POME on composite

Parameter (mg/L)	Pseudo-first order			Pseudo-second order		
	K_1	$q_{e(\text{cal})}$ mg/g	R^2	K_2	$q_{e(\text{cal})}$ mg/g	R^2
COD	0.0552	682.57	0.9306	0.0013	370.37	0.9871
$\text{NH}_3\text{-N}$	0.0010	103.04	0.9362	0.0034	262.71	0.9895

4. Conclusion

In this study, the result of the batch study conducted using adsorbents investigated under different conditions revealed that the optimum reduction of COD and $\text{NH}_3\text{-N}$ from POME using hydrophobic surface was achieved at 15:25 cm^3 by volume of ACBP:ACSC while findings showed that the optimum reduction of COD and $\text{NH}_3\text{-N}$ on hydrophilic interface was achieved at 35 cm^3 volumetric dosage using zeolite. In addition, from the investigation, it was observed that under hydrophobic–hydrophilic conditions, the reduction of COD and $\text{NH}_3\text{-N}$ was best achieved at 25:15 cm^3 of volumetric dosage, respectively. Finally, the optimum condition for the preparation of composite from the investigated adsorbents was achieved at adsorbent–binder ratio of 80:20 which implies that least application of OPC is required to produce composite from activated coconut shells, activated cow bones and zeolite. This can be attributed to the influence of ACBP which is known to contain hydrating properties as a result of the presence of quick lime. Equilibrium data were fitted to the isotherm models and results obtained indicated a better fit using the Langmuir isotherm, this is an indication that the adsorption of $\text{NH}_3\text{-N}$ and reduction of COD as a result of the energies of adsorption was homogeneously distributed on a monolayer surface. Kinetic data also fitted better to pseudo-second order model for both COD and $\text{NH}_3\text{-N}$ which indicated that adsorption was chemisorptive. Furthermore, the mechanism of adsorption suggested that the adsorption of $\text{NH}_3\text{-N}$ and reduction of COD was not only a rate controlling step but is also influenced along the boundaries.

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