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Treatment of tropical stabilised landfill leachate using palm oil fuel ash: isothermal and kinetic studies

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abstract

Landfill leachate is a hazardous by-product of landfills which can lead to surface and groundwater contamination if not properly managed, bringing a series of adverse effects to the natural environment, welfare, and human health. Landfill leachate must be treated to meet the discharge standards before discharging to the environment. This study aimed to treat stabilised landfill leachate using palm oil fuel ash (POFA). The adsorbent used in this study was POFA activated via KOH (treated palm oil fuel ash (TPOFA.KOH)) with impregnation ratio of POFA:KOH equal to 1:1. Batch adsorption studies were conducted to evaluate the effect of contact time, shaking speed, and adsorbent dosage. Removal efficiencies of chemical oxygen demand (COD), colour, and ammoniacal nitrogen (NH_3–N) achieved in this study were 75.44%, 85.37%, and 18.68%, respectively. Isothermal study was conducted to examine the adsorption capacity of POFA by Langmuir and Freundlich models, whereas the kinetic study was conducted to examine the adsorption mechanism of POFA by pseudo-first and pseudo-second-order models. Consequently, the adsorptive removal of colour, COD, and NH_3–N onto POFA were favourably fitted to Langmuir isotherm with maximum adsorption capacities of colour, COD, and NH_3–N at 28.329 Pt-Co/g, 27.778, and 0.0508 mg/g, respectively, indicating that TPOFA.KOH has high adsorption capacity for organic compounds compared with NH_3–N. The kinetic data agreed satisfactorily with the pseudo-second-order which indicated that the adsorption process was controlled by chemisorption.

Keywords: Adsorption; Kinetics; Palm oil fuel ash; Stabilised landfill leachate; Waste management

1. Introduction

With the goal of Malaysia to become an industrialised and sustainable country, it is foreseeable that it faces some challenges regarding solid waste management. Malaysia is very dependent on landfills where most of wastes collected are delivered and disposed [1], regardless of the problems of landfill disposal. Despite the strong dependency on landfills with about 170 disposal landfill sites in use, there are only 14 sanitary landfills in Malaysia which were designed to protect from environmental pollution and health risk [2]. This is undoubtedly a disturbing situation as open dumping areas with overloaded capacity tend to pose serious environmental and social problems [3]. This is because landfill leachate can be produced as storm water percolates through layers of wastes in landfills. Landfill leachate is a dark colour wastewater. It contains high concentrations of

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dissolved or suspended organic and inorganic chemicals, nitrogen compounds, salts, and heavy metals that can infiltrate into soil and subsoil [4], which, if not treated, will result in severe environmental impacts such as water, groundwater, and soil pollution.

Landfill leachate can be classified into three types including young, intermediate, and stabilised leachate which can be affected by the factor of age of landfill [5]. As the landfill aging, the high biodegradability compounds in the young leachate will reduce and the leachate will transform into intermediate and stabilised leachate due to the presence of nonbiodegradable organic materials which are refractory compounds such as humic and fulvic-like fractions [6]. Stabilised landfill leachate (SLL) can be produced from landfills that are more than 10 y old which has low biochemical oxygen demand 5 (BOD5)/chemical oxygen demand (COD) ratio and high ammoniacal nitrogen (NH_3–N) [7]. Due to the lower amount of biodegradable compounds in stabilised leachate, physicochemical processes provide more reliable and effective treatment as compared with biological treatment in which adsorption is one of the most effective physicochemical processes [5].

Adsorption is a surface phenomenon at which the molecules of a medium, which is usually liquid (adsorbate), are attracted and retained on the surface of the other medium, which is usually solid (adsorbent). Since the mechanism is occurring on the surface of the adsorbent, a high surface area of adsorbent is required to increase the effectiveness of the treatment. Common adsorbents are activated carbon (AC), zeolite, limestone, chitosan, chitin, activated alumina, and peat [8]. There are two categories of adsorption which are physisorption, which involves the van der Waals forces of attraction as physical bonding, and chemisorption, which depends on the force of the chemical bonding. Physisorption is reversible by heating or reducing pressure as the force of attraction is weak. In addition, the other characteristic of physisorption is that the molecules of adsorbate are accumulated and form multilayers. On the other hand, chemisorption cannot be easily reversible as the forces of attraction between adsorbate and adsorbent are very strong. Besides, the molecules of adsorbate are accumulated and form monolayers in the process of chemisorption [9]. However, the bottleneck of utilising adsorption via AC for leachate treatment process is the high production cost and expensive carbonaceous materials involved. Thus, the use of nonconventional and cost-effective materials such as industrial by-products and agriculture food wastes that are locally available can partially resolve the problem [10]. These materials can be chemically modified and used as a low-cost adsorbent for landfill leachate treatment. The present study focuses on examining the potential usage of unwanted abundant amount of palm oil fuel ash (POFA) for the first time to treat leachate generated from mature anaerobic landfill. POFA is one of the latest additions to the ash family, which is obtained from burning palm oil husks and palm kernel shells as fuel in palm oil mill boilers. In general practice, this ash is thrown away near the milling area and creates pollution [11]. As a second largest palm oil producer and exporter in the world, Malaysia generates POFA at an enormous and increasing quantity as palm oil mills are developing throughout nation [12]. In the burning process, there is about 5% POFA by weight of solid wastes being produced [13]. Therefore, utilising POFA as an adsorbent to treat landfill leachate, if effective and practical, is a solution to one of the largest environmental problems in Malaysia.

2. Materials and methods

2.1. Sample collection

SLL samples were collected from Sahom landfill (4°23′25″N, 101°10′57″E), located at Jalan Sahom, Kampar district, Perak, Malaysia. After the collection of Sahom landfill leachate (SLL), the sample was immediately transported back to Environmental Laboratory (EV-Lab), Faculty of Engineering and Green Technology, UTAR, Kampar, and stored at 4°C to minimise any chemical reactions and the biodegradation of the leachate sample [14]. POFA was collected from Tian Siang Oil Mill (Air Kuning) Sdn. Bhd., which has the location of 4°9′42″N, 101°9′36″E.

2.2. Pretreatment of POFA

POFA has a grey colour, and with increasing proportions of unburnt carbon, it becomes darker. The particles are relatively spherical with a wide range of sizes. The chemical composition indicates that POFA contains 62.6% SiO_2, 9.05% K_2O, 8.12% Fe_2O_3, 5.7% CaO, 4.65% Al_2O_3, 3.52% MgO, and 1.16% SO_3 [11]. The specific gravity of POFA was found to be 2.42 [11]. This study used POFA activated via KOH (treated palm oil fuel ash (TPOFA.KOH)) at an impregnation 1:1 ratio of POFA:KOH. The POFA was immersed in chemical for 2 h [15]. It was then rinsed thoroughly with deionised water until the pH stabilised. The sample was dried in an oven at a temperature of 105°C for 24 h to eliminate the moisture content. Then, the treated POFA was ground and sieved to a particle size of 500 μm. This was done to exclude coarser and unwanted materials, reduce the POFA particle size, and thus increase its surface area and improve the reactivity.

2.3. Experimental setup and run – adsorption

In this study, the treatment of SLL was done by adsorption using POFA as an adsorbent. A leachate sample of 100 mL was transferred to a 250 mL conical flask, followed by addition of POFA into the leachate sample where the parametric effects of the POFA dosage, shaking speed, and contact time were investigated. The sample was gently mixed and fixed to the Orbital Shaker, NB-101M, Korea. The desired shaking speed was set in the unit of rpm, and the orbital shaker was run with a desired contact time. Later, as the shaking process was stopped, POFA was filtered out of the SLL and the characteristics of the treated leachate were analysed and compared with the initial characteristics. The percentage of removal of pollutant in the aqueous solution was calculated using Eq. (1).

$$\text{Percentage pollutant removal } \left(\%\right) = \frac{\left(C_0 - C_e\right)}{C_0} \times 100 \quad (1)$$

where C_0 = initial concentration of the pollutant; C_e = final concentration of the pollutant

2.4. Batch Adsorption Studies

Studies of adsorption in batch mode were carried out to investigate the effect of the parameters on the TPOFA. KOH-treated leachate sample, including contact time, shaking speed, and TPOFA.KOH dosage. The contact time of the adsorption process was manipulated at 0, 15, 30, 60, 120, 180, 240, 360, and 480 min, with the same shaking speed and TPOFA.KOH dosage of 250 rpm and 2 g/100 mL SLL, respectively. To determine the effect of shaking speed, the adsorption process was carried out with different shaking speed at 0, 10, 30, 50, 100, 200, and 250 rpm [10]. All of the adsorption process for all of the samples were carried out with the constant TPOFA.KOH dosage of 2 g/100 mL SLL and optimum contact time obtained. The effect of adsorbent dosage was examined at 0.0, 0.1, 0.3, 0.7, 1.0, 1.5, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, and 10.0 g of TPOFA.KOH.

2.5. Isothermal study

Equilibrium isotherms of the adsorption characteristics including the type of surface, capacity, intensity, and energy of the adsorbent (POFA) on the adsorbate (SLL) were studied by Langmuir and Freundlich isotherm models [16]. Langmuir isotherm describes the efficiency of the adsorbent in the adsorption mechanism with the plot of amount of impurity adsorbed by adsorbent (POFA) against the amount of the impurity remains in the adsorbate (SLL). Langmuir model assumes that the adsorbent surface had fixed numbers of accessible sites which are homogeneously available on monolayer surface where each site can accommodate only one molecule [17]. There is a fixed area for each site of adsorbent that is quantified by the geometry of the surface, with the same adsorption energy at all the sites [18]. According to Metcalf & Eddy [19], the linear form equation of Langmuir isotherm is shown in Eq. (2).

$$\frac{1}{q_e} = \frac{1}{QK_L C_e} + \frac{1}{Q} \quad (2)$$

where q_e = mass of adsorbate adsorbed per unit mass of adsorbent (mg/g), Q = the maximum monolayer adsorption capacity (mg/g), K_L = Langmuir constant (L/mg), C_e = equilibrium concentration of adsorbate in solution after adsorption (mg/L).

In Freundlich isotherm model, it is assumed that heterogeneous surfaces favour the adsorption process at multilayer which is composed of various classes of adsorption sites [20]. According to Metcalf & Eddy [19], the linear form equation of Freundlich isotherm is shown in Eq. (3), where K_f and $1/n$ are represented by the intercept and slope of log q_e against log C_e plot, respectively [20].

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \quad (3)$$

where C_e = equilibrium concentration of adsorbate in solution after adsorption (mg/L), q_e = mass of adsorbate adsorbed per unit mass of adsorbent (mg/g), K_f = Freundlich constant, adsorption capacity indicator (mg/g) (mg/L), $1/n$ = Freundlich constant, adsorption intensity indicator.

2.6. Kinetic study

A kinetic adsorption study was carried out to study the adsorption efficiency of the POFA for landfill leachate treatment. According to Bashir et al. [21], kinetic modelling is commonly used to investigate the adsorption mechanism and the potential rate of the controlling process such as mass transfer and chemical adsorption. The pseudo-first-order and pseudo-second-order models are the most common used kinetic models in water and wastewater treatment [16]. Pseudo-first-order kinetic model is used to describe a reversible adsorption reaction, namely, physisorption, which was being established with an equilibrium relation between liquid and solid phases [22]. This model suggests that the rate of the reaction is proportional to the concentration of the contaminant. The pseudo-first-order equation based on Aziz et al. [23] is shown in Eq. (4).

$$\log\left(q_e - q_t\right) = \log\left(q_e\right) + \frac{K_1 t}{2.303} \quad (4)$$

where q_e = total adsorbed pollutants at equilibrium (mg/g for COD and Pt-Co/g for colour), q_t = amount of adsorbate adsorbed at time t (mg/g), K_1 = equilibrium rate constant of pseudo-first-order kinetic model (min^{-1}).

Pseudo-second-order kinetic model suggests that the surface adsorption is controlled by chemisorption where the removal occurs due to the physicochemical interaction between the solids, which normally are adsorbates, and liquids, which normally are adsorbents [10]. The pseudo-second-order equation based on Aziz et al. [23] is shown in Eq. (5).

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

where q_e = total adsorbed pollutants at equilibrium (mg/g for COD and Pt-Co/g for colour), q_t = amount of adsorbate adsorbed at time t (mg/g), K_2 = equilibrium rate constant of pseudo-second-order kinetic model (g/mg min).

2.7. POFA characterisation

The properties of the POFA obtained under optimal preparation conditions were determined by several analysis methods. The Fourier transform infrared spectroscopy (FTIR) was used to qualitatively identify the chemical functionality of TPOFA.KOH where the FTIR spectra were recorded between 4,000 and 400 cm^{-1}. Meanwhile, the surface physical properties of POFA were characterised with Micromeritis ASAP, 2020, using N_2 as the adsorbate at 77 K. The thermogravimetric analysis (TGA) was conducted by thermogravimetric analyser to determine the moisture content, fixed carbon, volatile matter, and ash contents of the sample by measuring the mass changes of sample at different stages of heating.

3. Results and discussions

3.1. Sample characteristics

Table 1 shows the characteristics of leachate sourced from Sahom landfill located in Perak, Malaysia. Leachate characteristics can be represented by several parameters including BOD_5, COD, colour, NH_3–N, turbidity, and pH. Based on the results shown in Table 1, Sahom landfill leachate is categorised as SLL as the BOD_5/COD ratio is less than 0.1 [7].

Table 1
Raw leachate sample characterisation

Parameter	Value range	Malaysia discharge standards
Dissolved oxygen, mg/L	2.43–5.19	–
BOD_5, mg/L	55–122	20
COD, mg/L	846–1,530	400
BOD_5/COD	0.065–0.080	–
Colour, Pt-Co/L	1,040–1,680	100
NH_3-N, mg/L	164–462	5
Turbidity, NTU	15.9–70.2	–
pH	7.97–8.68	6.0–9.0
Temperature, °C	27.7	–
Suspended solids, mg/L	75.0	50
Electrical conductivity, mS	13.22–22.77	–

The other factors indicate that the SLL is in the methanogenic phase as COD concentration is relatively low and pH > 8 [24]. The chemical composition reveals that POFA contains low calcium oxide, significant amount of silica, aluminium, iron, magnesium, potassium, and sulphur [11,25], where the specific gravity and Blaine fineness of POFA were found to be 2.42 and 4,930, respectively [26].

3.2. Batch adsorption studies

3.2.1. Effect of contact time

The effect of contact time on the removal efficiencies of COD, colour, and NH_3–N is shown in Fig. 1, together with their respective effluent concentrations. At this stage, the effect was studied using 2 g of TPOFA.KOH to treat 100 mL SLL with a range of contact time from 0 to 480 min at constant shaking speed of 250 rpm. Based on Fig. 1, the percentage removal of COD, colour, and NH_3–N increased as the contact time increased and became relatively stable after 180 min. It can be seen that the effluent concentrations in terms of COD, colour, and NH_3–N dramatically decreased and became relatively stable after the contact time of 180 min. This shows that the optimum removal efficiencies were obtained at 180 min, and the results for COD, colour, and NH_3–N were 43.17%, 41%, and 8.51%, respectively. Note that there was no significant improvement on the removal efficiency of NH_3–N as the contact time increased. This is because the removal of NH_3–N by TPOFA.KOH was low although the optimised adsorption conditions were achieved. According to Halim et al. [20], similar low adsorption capabilities of AC on NH_3–N were observed due to its hydrophobic surface. As the contact time varied from 0 to 480 min, the removal percentage increased with time, and equilibrium was not attained as the removal efficiencies had increased continuously. The results showed that the adsorption capacity was higher in the early stage (from 15 to 180 min), indicating that the available surface sites of POFA were larger. However, with the constant amount of POFA/TPOFA and shaking speed, as the contact time was beyond 180 min, the adsorption efficiency

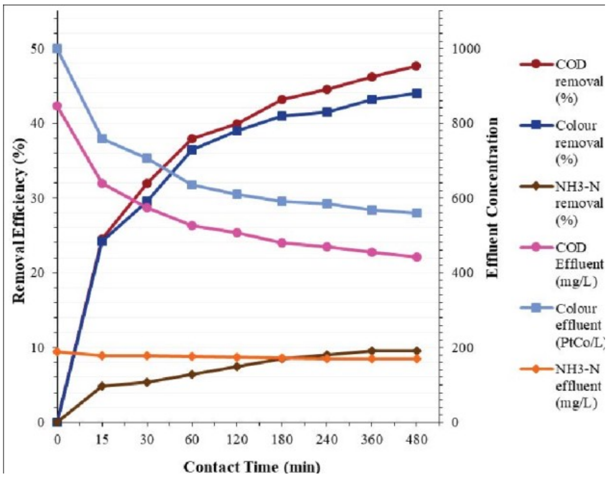


Fig. 1. Effluent removal efficiency for treatment parameter of contact time.

had become relatively stable and close to the equilibrium at which the availability of sorption site would decrease and become difficult to be occupied due to the repulsion forces between the solute molecules on the solid and bulk phase [27]. Therefore, the continuous studies on the effects of shaking speed and dosage of adsorbent were carried out using the optimum contact time obtained, which was 180 min (3 h).

3.2.2. *Effect of shaking speed*

The effect of shaking speed on the removal efficiencies of COD, colour, and NH_3–N is demonstrated in Fig. 2. The effect was studied using 2 g of TPOFA to treat 100 mL SLL with a range of shaking speed from 0 to 250 rpm at constant (optimum) contact time of 180 min. Based on Fig. 2, the percentage removal of COD, colour, and NH_3–N increased as the shaking speed increased, and became relatively stable at 100 rpm onwards, to 250 rpm. It can be observed from Fig. 2 that the reduction on the effluent concentrations of COD, colour, and NH_3–N was relatively steady but slowly increasing. Note that the removal efficiencies of COD, colour, and NH_3–N increased as the shaking speed increased as the shaking process provides mixing with higher probability of contact between the adsorbate (SLL) and adsorbent (TPOFA) which improved the treatment efficiency. Due to the limitation of speed of orbital shaker, the maximum removal efficiencies were obtained at 250 rpm, and the results for COD, colour, and NH_3–N were 43.96%, 44.76%, and 7.60%, respectively. Therefore, the continuous studies on the effect of dosage of adsorbent were carried out using the optimum contact time of 3 h as well as shaking speed of 250 rpm.

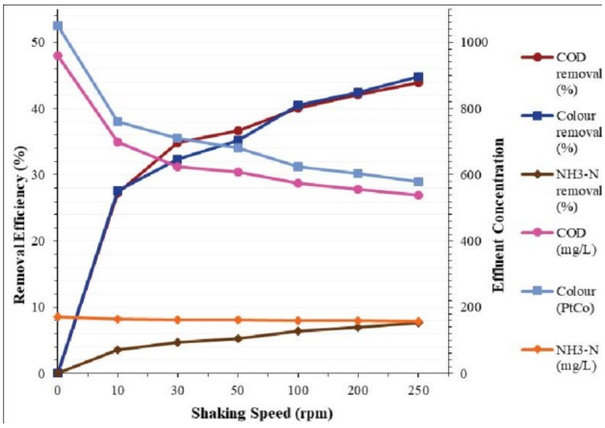


Fig. 2. Effluent removal efficiency for treatment parameter of shaking speed.

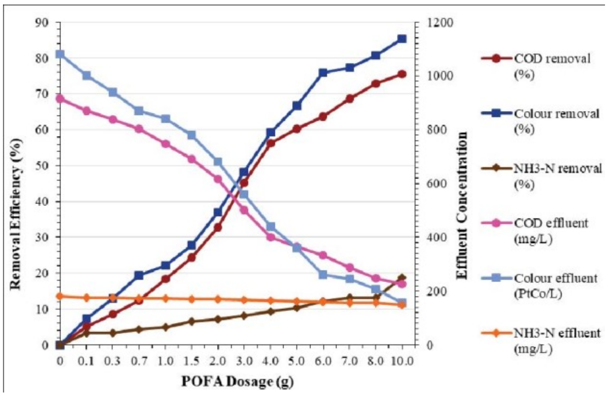


Fig. 3. Effluent removal efficiency for treatment parameter of POFA dosage.

3.2.3. *Effect of adsorbent (TPOFA.KOH) dosage*

The effect of adsorbent dosage on the removal efficiencies of COD, colour, and NH_3–N is demonstrated in Fig. 3. The effect was studied using a range of TPOFA amount to treat 100 mL of landfill leachate with a constant contact time of 180 min and constant shaking speed of 250 rpm. Based on Fig. 3, the percentage removal of COD, colour, and NH_3–N increased as the dosage of POFA increased. Therefore, the highest removal efficiencies of COD, colour, and NH_3–N using 10 g of POFA were 75.44%, 85.37%, and 18.68%, respectively. Nevertheless, by using 5 g POFA/100 mL landfill leachate, the removal efficiencies for COD, colour, and NH_3–N were 60.26%, 66.67%, and 10.44%, respectively. A steady decrease in adsorption uptake can be seen at high adsorbent dosage due to the unsaturated adsorption sites [21,28]. It is expected that the adsorption efficiency will still increase but with a very low rate and finally reach an equilibrium as the dosage of POFA increases. This expectation is made as there will be overlapping of adsorption sites occurring due to the overloading of adsorbent.

3.3. *Isothermal and kinetic studies*

3.3.1. *Isothermal study*

Isothermal study is an equilibrium-based study on adsorption process on surfaces [20]. Based on the experimental data of effect of TPOFA dosage in batch adsorption studies, the Langmuir and Freundlich isotherm models of POFA for colour, COD, and NH_3–N are shown in Figs. 4 and 5, respectively. For the Langmuir isotherm, the constant Q was evaluated from the slope, whereas K_L was determined from the intercept as demonstrated in Fig. 4. For the Freundlich isotherm, the plot of log q_e vs. log C_e gives a straight line with slope $1/n$. The K_f value was obtained from the intercept value as shown in Fig. 5.

The values of Q, K_L, and the linear regression correlation (R^2) for colour, COD, and NH_3–N based on Langmuir model as well as the K_f, $1/n$ values, and the linear regression correlation (R^2) for colour, COD, and NH_3–N based on Freundlich model were tabulated and shown in Table 2. Based on Table 2, the adsorption capacities of POFA obtained from Langmuir model for colour, COD, and NH_3–N were 28.329 Pt-Co/g, 27.778, and 0.0508 mg/g, respectively, indicating that POFA has high adsorption capacity in organic compounds but low in NH_3–N.

In Freundlich isotherm, $1/n$ was calculated to study the adsorption intensities of POFA. According to Kucic et al. [29], the result of $1/n$ can determine whether the adsorption process is in favourable ($1/n < 1$) or unfavourable ($1/n > 1$) conditions. Due to $1/n > 1$, increase in adsorption constant was noted as the solution concentration increases, which indicates the rise in hydrophobic properties of the surface after monolayer formation [10,16]. Based on Table 2, the results of $1/n$ of the parameters of colour and COD were less than 1, specifically 0.4947 and 0.5320, respectively. This shows that colour and COD removals were achieved in POFA adsorption. However, the result of $1/n$ of NH_3–N was 11.391 which is more than 1, indicating that the removal of NH_3–N was not achieved. In addition, adsorption capacity can be indicated by the K_f value, and higher K_f shows higher adsorption capacity of adsorbents towards the pollutants [30]. Results in Table 2 show that the colour parameter obtained the highest K_f which was 0.7881, followed by COD and NH_3–N which were 0.4838 and 3.4119E-26, respectively. The adsorption of colour,

COD, and NH_3–N is rationally explained by Langmuir and Freundlich isotherms. In fact, both isotherm models obtained high R^2 values ($R^2 > 0.9$); thus, both isotherms were applicable. However, the Langmuir model yielded relatively higher R^2 values for all of the parameters including colour, COD, and NH_3–N. Similar trend was observed for the adsorption of colour, COD, and NH_3–N by sugarcanes bagasse and coffee ground-ACs [24,27]. The validity of the Langmuir isotherm model suggested that the adsorption of colour, COD, and NH_3–N onto POFA is monolayer with each molecule having equal enthalpies and activation energy [17].

3.3.2. Kinetic study

The experimental efficiency is controlled by the kinetic adsorption at which the kinetic modelling is normally used to investigate the mechanism of adsorption and the potential rate controlling the process such as mass transfer and chemical reaction [31]. Based on the experimental data, the adsorption kinetics of colour, COD, and NH_3–N for pseudo-first-order model and pseudo-second-order model were investigated as shown in Figs. 6 and 7.

Table 3 shows the results of overall $q_{e,\mathrm{exp}}$, $q_{e,\mathrm{cal}}$, K_1, and R^2 for pseudo-first-order kinetic model, $q_{e,\mathrm{cal}}$, K_2, and R^2 for pseudo-second-order kinetic model. The values of R^2 for parameters of colour, COD, and NH_3–N were compared within the two models. Based on Table 3, the values of R^2 obtained from

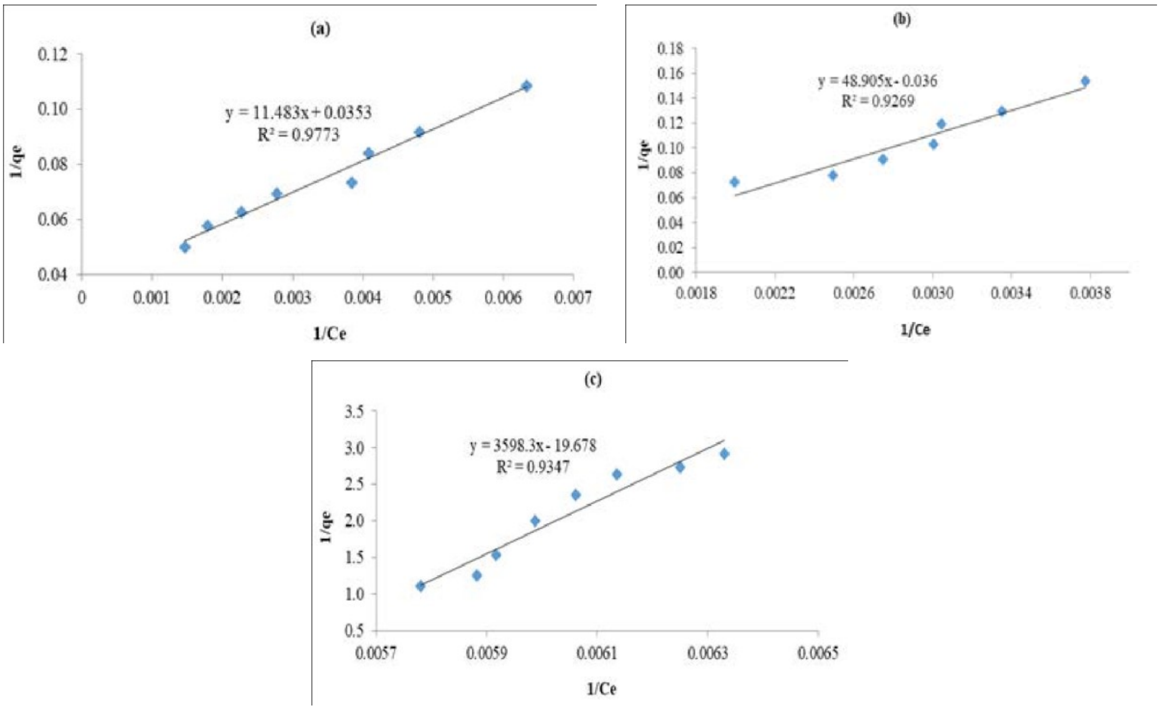


Fig. 4. Langmuir isotherm for adsorptive removal of (a) colour, (b) COD, and (c) NH_3–N.

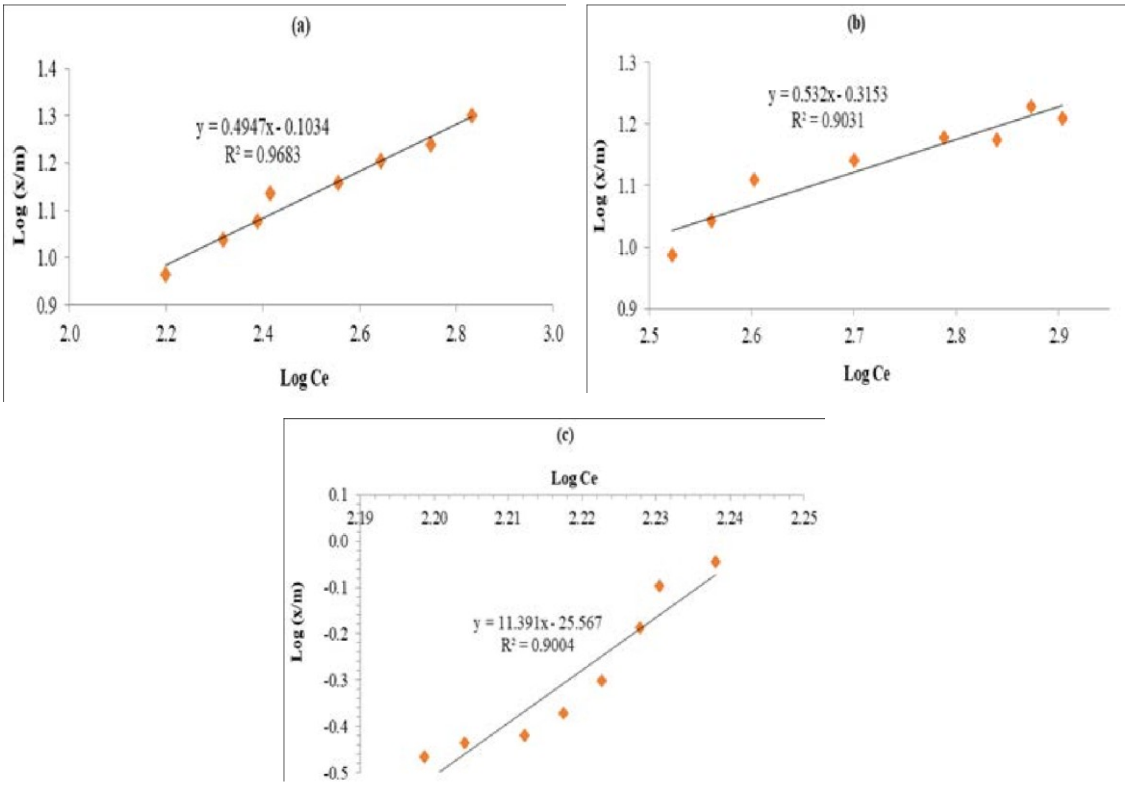
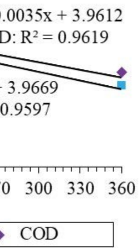


Fig. 5. Freundlich isotherm for adsorptive removal of (a) colour, (b) COD, and (c) NH_3–N.

Table 2
Isotherm equation parameters for colour, COD, and NH_3–N adsorption onto POFA

	Langmuir isotherm coefficient			Freundlich isotherm coefficient		
	Q		R^2	K_f mg/g ((L/mg) 1/*n*)		R^2
Parameter		K_L (L/mg)			1/*n*	
Colour	28.329 (Pt-Co/g)	0.0000802	0.9773	0.7881	0.4947	0.9683
COD	27.778 (mg/g)	0.0000898	0.9269	0.4838	0.5320	0.9031
NH_3–N	0.0508 (mg/g)	0.1192606	0.9347	3.4119E-26	11.391	0.9004

Fig. 6. Pseudo-first-order kinetic model of POFA for colour, NH_3–N, and COD.



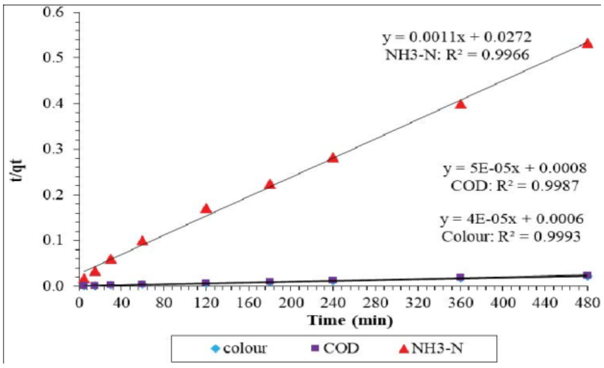


Fig. 7. Pseudo-second-order kinetic model of POFA for NH_3–N, colour, and COD.

pseudo-first-order kinetic model for parameters of colour, COD, and NH_3–N were 0.9597, 0.9619, and 0.9900, respectively, whereas the values of R^2 obtained from pseudo-second-order kinetic model for parameters of colour, COD, and NH_3–N were 0.9993, 0.9987, and 0.9966, respectively. This indicates that the pseudo-second-order kinetic model held higher R^2 values for all parameters as compared with pseudo-first-order kinetic. In addition, the calculated equilibrium sorption capacities ($q_{e,\mathrm{cal}}$) of pseudo-second-order kinetic model also agreed well with experimental data ($q_{e,\mathrm{exp}}$). According to Bashir et al. [21], adsorption reaction by the pseudo-second-order model indicated that the sorption processes of pollutants were controlled by chemisorption. As pseudo-second-order model was more favourable as opposed to pseudo-first-order model, it showed that the adsorption process for colour, COD, and NH_3–N was controlled by chemisorption.

Table 3
Pseudo-first- and Pseudo-second-order kinetic models for POFA

Parameter	Exp	Pseudo-first-order model			Pseudo-second-order model		
	$q_{e,\mathrm{exp}}$ (μg/g)	K_1 (min$_{-1}$)	$q_{e,\mathrm{cal}}$ (μg/g)	R_2	K_2 (g/μg min)	$q_{e,\mathrm{cal}}$ (μg)	R_2
Colour	22,000	0.00898	9,266.16	0.9597	0.00002667	25,000	0.9993
COD	20,125	0.00806	9,145.34	0.9619	0.000025	20,000	0.9987
NH_3–N	900	0.00990	570.30	0.9900	0.004033	909.09	0.9966

4. Characterisation of POFA and TPOFA.KOH

4.1. FTIR analysis

The types of chemical bonding characteristics of the adsorbents can be identified by carrying out FTIR analysis [32]. The FTIR spectra of the original POFA and alkali-activated POFA (TPOFA.KOH) before and after adsorption process were recorded between 400 and 4,000 cm^{-1} as shown in Fig. 8. Based on Fig. 8(c), the characteristic bands are observed in the spectrum of original POFA at wavelengths 3,448, 2,371, 2,345, 1,637, 1,384, 1,100, and 474 cm^{-1}, whereas the TPOFA. KOH before and after adsorption has some differences in the wavelengths.

As shown in Fig. 8, diagnostic bands at both 3,448 and 2,345 cm⁻¹ appeared for all infrared spectra, whereas the wave number 2,371 cm⁻¹ appeared at spectrum of original POFA shifted to 2,367 cm⁻¹ in the spectrum of TPOFA.KOH before adsorption and to 2,363 in the case of TPOFA.KOH after adsorption. In addition, it can be clearly observed that the wave numbers 2,363 and 2,345 cm⁻¹ in the spectrum of TPOFA.KOH after adsorption have higher frequencies as compared with the other two spectrums. According to Naik et al. [33], strong diagnostic bands at 3,600–2,200 cm⁻¹ demonstrated the stretching of hydroxyl group (–OH) either as H–OH or Si–OH groups which attributed to the presence of cellulose and hemicellulose compounds [33]. After treated by KOH, the diagnostic bands at 2,367 and 2,363 cm⁻¹ for both of TPOFA.KOH before and after adsorption and at 2,345 cm⁻¹ of both of them became more obvious as compared with original POFA as there is more –OH contributed by KOH. Furthermore, the bending vibrations of wave number 1,384 cm⁻¹ at all of the spectra and 1,637 cm⁻¹ at spectrum of original POFA as well as wave numbers 1,636 and 1,629 cm⁻¹ at the spectrum of TPOFA.KOH before and after adsorption, respectively, demonstrate H–O–H bending [34]. The presence of this band shows that there are free water molecules attached on the surfaces of original POFA and TPOFA.KOH. The vibration spectra signaled at 1,100 cm⁻¹ in the spectrum of original POFA shifted to lower frequency at wave numbers 1,041 and 1,027 cm⁻¹ in spectrum of TPOFA.KOH before and after adsorption, respectively. Similarly, the wave number of original POFA at 474 cm⁻¹ shifted to 473 cm⁻¹ with lower frequency after KOH treatment, whereas it shifted to wave number 667 cm⁻¹ with lower frequency after adsorption. The 667 cm⁻¹ vibration shown in Fig. 8(a) is assigned to OH out-of-plane bending [35], which is attributed to the bending vibration mode of C–OH out-of-plane mode that may be stabilised because of the adsorbent materials adsorbed on the TPOFA.KOH surface [36].

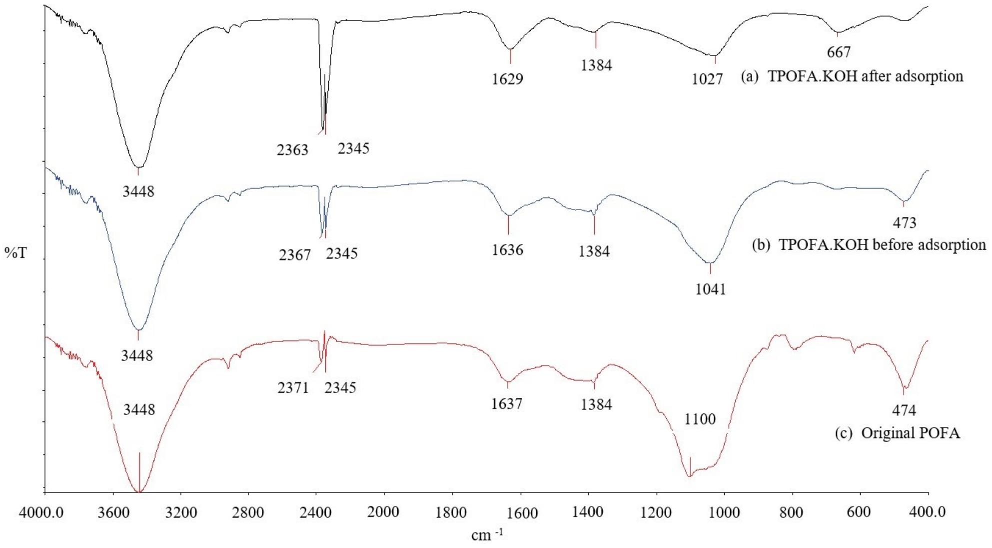


Fig. 8. FTIR spectra of original POFA and TPOFA.KOH before and after adsorption.

The broad bands around 1,100 and 1,041 cm⁻¹ are associated with the asymmetric stretching of Si–O–Si or Si–O–K bonds of SiO_2, whereas vibration modes at 474 and 473 cm⁻¹ attributed to the bending vibration mode of the Si–O–Si bonds of SiO_4. The transition in the wave numbers 1,100 and 474 cm⁻¹ to a lower wave number may be attributed to the transition of symmetric to asymmetric stretching mode of the Si–O–Si bonds. This transition may be followed by depolymerisation of silicate, and some substitution occurred for Si with K [37]. This shifting was understood as a penetration of K^+ atoms into the original arrangement of Si–O–Si skeletal structure. According to Davidovits [38], the formation of Si–O–K from the presence of K^+ and Si–O–Si can be initiated with the cleavage of the siloxane oxygen in Si–O–Si through transfer of the electron from Si to O, leading to the formation of intermediate silanol Si–OH on the one hand and basic siloxo Si–O– on the other hand. Followed by this is the further formation of silanol Si–OH groups and isolation of the ortho-sialate molecule, the primary unit in geopolymerisation. Then, the reaction of the basic siloxo Si–O– with the potassium cation K^+ leads to the formation of Si–O–K.

Properties	Raw POFA	TPOFA.KOH
BET surface area (m²/g)	172.9762	332.8742
Single-point surface area (m²/g)	175.1408	341.7063
Langmuir surface area (m²/g)	232.5961	442.0201
Micropore volume (cm³/g)	0.094775	0.224513

4.2. Pore structural characteristic

Table 4 summarises the pore structural characteristics in terms of Brunauer–Emmett–Teller (BET) surface area, Langmuir surface area, and micropore volume of POFA before and after treatment by KOH. From the data, it can be indicated that the porosity of TPOFA.KOH was greatly improved during activation stages.

4.3. Thermogravimetric analysis

Fig. 9 shows the results of TGA of both the original POFA and alkali-activated POFA (TPOFA.KOH) after adsorption, which are obtained within the temperature range of 30°C–1,000°C. At the first stage, complete dehydration was achieved by heating the samples at 30°C–110°C. The weight loss at this stage is due to release of moisture content. The volatile matters and fixed carbon contents were determined by the weight losses after the dehydration stage and oxidation stage, respectively. Lastly, ash was determined as the mass of the residue at the end of the analysis [39].

Table 4
Pore structural characteristic of POFA

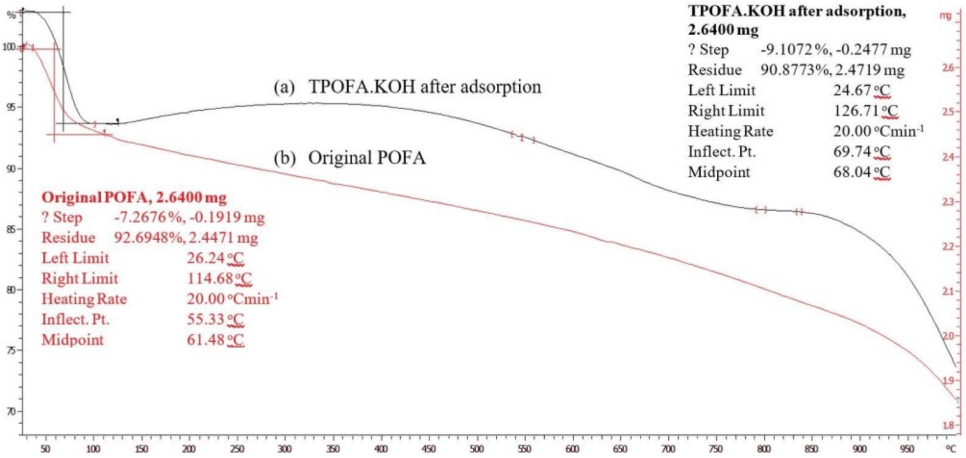


Fig. 9. Results of thermogravimetric analysis (TGA) of TPOFA.KOH after adsorption and original POFA.

Based on Fig. 9, the initial samples' weight of TPOFA.KOH after adsorption and the original POFA were 2.72 and 2.64 mg, respectively. These weights decreased to around 2.48 and 2.42 mg, respectively, at 30°C–110°C. The weight losses as moisture content are 0.24 mg for TPOFA.KOH after adsorption (Fig. 9(a)) and 0.22 mg for original POFA (Fig. 9(b)), which are equivalent to 8.82% and 8.33% of the total sample weight, respectively. After the dehydration stage, the weight loss of the sample at 110–550°C is due to the volatile matter content. Since the weight of TPOFA.KOH after adsorption was decreased from 2.48 to 2.43 mg, the weight loss as volatile matters is 0.05 mg which is equivalent to 1.84% of the total sample weight. Whereas the original POFA was decreased from 2.42 to 2.26 mg, the weight loss as volatile matters was 0.16 mg which is equivalent to 6.06% of the total sample weight. Further weight losses of 0.4 mg which is equivalent to 15.15% of the total TPOFA sample was fixed carbons form TPOFA.KOH after adsorption and the original POFA, respectively, as fixed carbons are thermally stable up to 550°C [40]. After the analysis, 1.93 and 1.86 mg of samples remained as ash which are equivalent to 70.96% and 70.45% of the total sample weight for post-adsorption and original sample, respectively. Therefore, the result of TGA shows that both TPOFA.KOH after adsorption and original POFA have low moisture, volatile matter, and fixed carbon contents but high ash contents.

5. Conclusions

In the study of treatment of SLL by adsorption where SLL acts as adsorbate and TPOFA.KOH with impregnation ratio 1:1 as adsorbent, removal efficiencies of COD, colour, and NH_3–N achieved throughout this study were 75.44%, 85.37%, and 18.68%, respectively. This was achieved using 10 g of POFA to treat 100 mL leachate, and the contact time of POFA and leachate was controlled at 3 h with shaking speed of 250 rpm. Based on the result of isothermal study, the validity of the Langmuir isotherm model suggested that the adsorption of colour, COD, and NH_3–N onto TPOFA.KOH is monolayer with each molecule having equal enthalpies and activation energy. The adsorption capacities of TPOFA.KOH obtained from Langmuir model for colour, COD, and NH_3–N were 28.329 Pt-Co/g, 27.778, and 0.0508 mg/g, indicating that TPOFA.KOH has high adsorption capacity in organic compounds but low in NH_3–N. In addition, the result of kinetic study shows that the pseudo-second-order model was more favourable as opposed to pseudo-first-order model, thus the adsorption process for colour, COD, and NH_3–N was controlled by chemisorption. From the results of characterisation of POFA and TPOFA.KOH, FTIR analysis shows that the diagnostic bands of TPOFA.KOH at 2,367 and 2,345 cm^{-1} became more obvious as compared with POFA as there are more hydroxyl groups (–OH) contributed by KOH, whereas TGA shows that POFA has low moisture, volatile matter, and fixed carbon contents which are 8.33%, 6.06%, and 15.15%, respectively, but high ash content which is 70.45%. Using wastes as raw materials, this treatment provides a vivid resolution to the two of the largest wastes in Malaysia which are landfill leachate and POFA.

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