Application of Palm Kernel Shell Granular Filter Medium for Decolourisation and COD Removal from Clarified Palm Oil Mill Effluent

Eric Awere*, Peter Appiah Obeng, and Alessandra Bonoli

***Abstract*—Palm oil mill effluent (POME) is characterised by high colour, COD and solids. Extraction and drying of the suspended solids for reuse as solid fuel shows great promise. However, the clarified wastewater may require further treatment to meet discharge limits. This study was aimed at evaluating the efficiency and kinetics of COD and colour removal from clarified POME using palm kernel shell (PKS) granular filter media and a sand filter as reference. The wastewater was collected from a small-scale palm oil processing mill in the Abura Aseibu Kwamankese District of Ghana and clarified using a solid-liquid separation system. The filter media of particle size 1.18mm was packed into acrylic cylinders (6cm dia.) to a height of 35.4 cm. The characteristics of influent wastewater and filter media were determined prior to the experiment following standard methods. Each filter was run as a batch system under anaerobic conditions by maintaining a minimum supernatant height of 10cm. Effluents were drawn from the bottom of each filter after 0, 24, 48, 72, 96, and 120 h for analysis using standard analytical methods. The removal efficiencies for the PKS and sand filters were, respectively, 77% and 79% for COD and 69% and 62% for colour. The COD removal was consistent with first-order kinetics for both PKS and sand filters. However, colour removal in PKS and sand filters followed second- and zero-order kinetics respectively. The correlation coefficients of the selected kinetic models show a strong correlation between the experimental and predicted results. Further research is required to establish the retention time required to bring the pollutant levels below the allowable limits for discharge into the environment.**

***Index Terms*—COD removal efficiency, colour reduction, kinetic model, palm kernel shell filter, palm oil mill effluent**

I. Introduction

Palm oil has attracted greater attention on the global commodities market due to factors such as its high yields relative to other edible oil crops, high demand for domestic and industrial purposes, use as a biofuel [1], and the need for cheaper sources of oleo chemicals [2]. Palm oil production accounted for around 35% of worldwide vegetable oil production in 2019 [3]. Palm oil production originated in Africa's tropical rain forest and equatorial region. However, Asia is currently the world's main producer and exporter of palm oil, with Indonesia, Malaysia, and Thailand leading the way [4], followed by Africa. For the year 2020, palm oil production in Africa and West Africa represented respectively 3.1% and 4% of the global output [5].

Oil palm is harvested as fresh fruit bunches (FFB). A tonne of fresh fruit bunches is composed of 230–250 kg of empty fruit bunches (EFB), 130–150 kg of fibres, 60–65 kg of palm kernel shells (PKS), 55–60 kg of palm kernels, and 160–200 kg of unrefined oil [6]. The extraction of oil involves several techniques that differ in terms of the level of mechanisation and interconnected material transfer mechanisms. In Africa, processing is undertaken at four distinct scales: traditional-scale, small-scale, medium-scale, and large-scale [7]. The traditional-scale processors employ largely manual procedures. The small-scale processors use inefficient stand-alone machines to digest and press fruits. The medium- and large-scale processing mills use technologically up-to-date machinery, established by agro-industrial complexes. Small-scale processing mills are mostly located in rural areas and small towns and belong to the informal sector, with inadequate capital and credit [8]. Their adherence to legal and environmental regulations is relatively weak.

Even though they can only mill a small amount of oil at a time, small-scale mills account for up to 83% of all palm oil production in Africa [9]. Small-scale palm oil processing involves the receipt of fresh fruit bunches, splitting, storage, stripping, fermentation, boiling, digestion/pressing, and clarification. Detailed information on the palm oil production processes may be obtained from our earlier publication [10]. Water is used at various stages of the production process, each of which generates palm oil mill effluent (POME). Processing fresh palm fruits into crude palm oil generates waste products (EFB, PKS, palm fibre, and POME) whose quality and quantity depend on factors such as the type and grade of palm fruits used, as well as the processing technique employed [11]. It is reported that, for every tonne of palm oil produced, 5.0–7.5 tonnes of water are consumed, with 50%–79% returning as POME [12]. Similarly, the POME return factor for small-scale processing mills is 72%–75% in Nigeria [13] and 68%–82% in Ghana [14].

POME is an odorous, non-toxic, viscous, and brownish liquid with a high water content (95%–96%), unrecovered oils (0.6%–0.7%), and suspended solids from the fruit debris (2%–4%). It has a low pH because of the organic and free fatty acids produced by the partial breakdown of palm fruits prior to processing. The brownish colour is caused by the presence of carotene, pectin, tannin, phenolic acid, and lignin, which make POME a nutrient-rich substance [15] but may have a negative impact on the receiving environment if

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discharged without adequate treatment [16]. Table I shows the characteristics of POME from small-scale palm oil processing mills in Ghana and Nigeria as well as industrial-scale mills in Asia.

TABLE I: CHARACTERISTICS OF PALM OIL MILL EFFLUENT

Parameter	Small-scale mills		Industrial scale mills	
	Awere *et al.* [10]	Ewelike *et al.* [17]	Mahmod *et al.* [18]	Yap *et al.* [19]
pH	4.61–4.74	4.8	4.1–5.2	3.78–4.95
TS	2,569–5,327	-	40,000	-
TDS	211–551	-	-	-
TSS	2,070–5,106	8,300	5,000–54,000	44,957–161,833
BOD_5	16,172–27,888	29,500	10,250–43,000	40,717–73,412
COD	50,391–60,544	42,200	15,000–100,000	86,692–122,094
Total Nitrogen	160–373	-	180–1,400	3,867–5,145
Phosphorus	43–90	-	94–131	1,432–3,270
Potassium	126–191	-	1,281–1,928	-
Oil and grease	321–792	7,200	130–18,000	11,650–13,117

TS – total solids; TDS – Total dissolved solids; TSS – Total suspended solids; BOD – Biochemical oxygen demand; COD – Chemical oxygen demand; All parameters are in mg/L except pH

According to numerous research studies, small-scale processing mills typically discharge their POME into the natural environment without any treatment [7, 10, 20–22]. Improper disposal of POME contaminates the receiving land, aquatic bodies, and air by emitting odour, and contributing to greenhouse gas emissions. This nutrient-rich but environmentally damaging wastewater requires appropriate management strategies.

Many technologies have been investigated for their ability to treat POME. Mohammad *et al*. [23] reviewed the literature on palm oil mill effluent treatment processes and found that while phytoremediation, microbial fuel cell techniques (generating electricity with the aid of microorganisms), and agro-waste-derived bio-adsorbents appeared to be more cost-effective, they were unable to achieve satisfactory results in lowering COD and BOD levels. One of the low-cost technologies that has shown great promise (for tropical, resource-constrained countries like Ghana) is the recovery of suspended solids in POME using EFB fibre, sun drying, and the use of the product as fuel or soil conditioner [24]. However, the effluent from the solid-liquid separation process does not meet the requirement for direct discharge into the environment. Numerous physicochemical treatment methods involving biological processes, bioadsorbents, membranes, and coagulants have been used to treat POME, but according to Mohammad *et al*. [23], no single process can be used as a stand-alone treatment method at the commercial scale. According to them, usage of these adsorbents and chemical coagulants seems uneconomical and impractical. There is still ongoing research to find ideal POME treatment methods [25].

Filter systems for on-site treatment of wastewater are fairly common in Ghana. Sand is the most often used filter media for treating water and wastewater [26] but activated carbon has gained popularity in recent decades. The relatively high cost and challenges associated with acquiring and maintaining sand and activated carbon filters have prompted the quest for alternative low-cost filter media [27, 28]. Materials with high porosity, high carbon content, and the potential for sustainable reuse or recycling such as charcoal, bark, and sawdust have received a lot of attention [29]. Palm kernel shell, a solid by-product and waste material from palm oil processing, is also gaining popularity. PKS is produced in large quantities and needs to be managed. It has a wide application including bioenergy, animal feed, water and wastewater treatment, and construction [30]. However, only a small portion of PKS gets reused in Africa, for instance, with the remaining being inappropriately disposed of. Investigations into their continued uses are ongoing. The ultimate and proximate compositions of PKS show that it has a carbon content of 50%, a hydrogen content of 7.5%, a nitrogen content of 3.3%, and a sulphur content of 0.09% [31]. Its particle density is 1383 kg/m^3, its mean pore size is 12.9 nm, and its pore volume is 0.0473 cm^3/g [32]. The elemental composition of PKS varies slightly based on plant species, location of plantations, and management activities [33]. The high carbon content and appreciable porosity make PKS a suitable material to be used as an adsorbent.

In most studies involving the utilisation of PKS, it has been prepared into activated carbon (granular or powdered) prior to its usage [34–39]. In the activated form, PKS has high porosity and surface area compared to non-activated PKS [40]. Consequently, activated PKS media is expected to achieve a higher pollutant removal than the non-activated PKS media. PKS activated carbon has also been used as an adsorbent to remove specific pollutants from surface water and grey water [41], heavy metals from wastewater [42], dye removal [36], carbon dioxide capture [43, 44], nitrogen dioxide, and ammonia removal [45]. But few studies have used non-activated PKS for water and wastewater treatment applications. Ogedengbe [46] used charred and uncharred palm kernel shells as granular filter media (particle size of 0.85-2.36 mm; porosity of 0.46) for reduction of turbidity in water. The author concluded that uncharred PKS holds great potential as granular filter media for wastewater treatment. Similarly, Budari *et al*. [47] tested the performance of burnt PKS in a single and dual media bed column experiment for the removal of total coliforms and Escherichia coli from raw water. The single media filter achieved 0.11–0.27 log removal for total coliforms and 0.15–0.39 log removal for E. coli. A 100% removal of colour (of POME) from final pond effluent was achieved within 12 hrs using powdered activated carbon prepared from PKS by chemical and microwave methods [48]. A pilot-scale, two-stage, vertical-flow engineered wetland incorporated with PKS was used to remove nitrogen and ammonia from septage [49]. The wetland achieved satisfactory removal efficiencies for total nitrogen (83%), ammonia (97%), COD (94%), and BOD_5

(97%).

Despite the above applications, research on the use of non-activated PKS as a granular bed filter material for wastewater treatment is restricted. The non-biodegradable property of PKS makes it a potential media for filtration. The objectives of this study were to determine the removal efficiency and kinetic models of COD and colour from clarified POME using PKS granular bed filter media.

II. Materials and Methods

A. Wastewater Sample Source and Preservation

Raw POME was collected from a small-scale palm oil processing mill located in the Abura Aseibu Kwamankese District of Ghana's Central Region on Longitude 1°12'19" West and Latitude 5°15'59" North. The POME was clarified using empty palm fruit bunch fibre (EFBF) as a solids-liquid separator to separate the solids (called sludge) from the liquid (referred to as the influent POME in this study). A detailed description of the solid-liquid separation setup, process and performance is reported in Awere *et al*. [24]. The influent POME from the solid-liquid separation processes was used for the current research.

The influent POME was stored under 4 °C in a refrigerator to inhibit microbial activities [50, 51] before use in the experiment. Prior to applying the influent POME in the filtration experiment, it was kept out of the refrigerator and allowed to reach room temperature.

B. Preparation and Characterisation of Filter Materials

The choice of PKS as filter media was influenced by its low cost and availability as locally generated waste from the crude palm oil extraction industry. A sand filter media was included as a reference because of its extensive use as filter media for the treatment of water and wastewater [28, 52]. River sand, commonly utilised for building construction in Ghana, was obtained in Cape Coast for this purpose. The PKS used in the current experimental set-up was obtained from the same processing mill where the POME sample was collected. The PKS was crushed using a mechanical crusher (Eberbach E3300, Michigan, USA). The PKS production process is summarised in Fig. 1. The filter materials (crushed PKS and sand) were cleaned to remove fine particles, silt, and other unwanted materials by soaking them in tap water for 24 hrs after which the water was drained. Subsequently, the media were thoroughly washed and oven-dried at 103 °C–105 °C for 2 h before characterisation.

The physical properties of the filter materials were determined following standard procedures for soil analysis [53]. The physical properties determined in this study were particle size and particle density, based on studies reported in literature [28, 52], and their relevance to the current study. The dry sieve method (BS 1377: Part 2: 1990) was used in evaluating the particle size. In determining the particle size, the media were sieved through a stack of sieves of sizes 600 µm, 1.18 mm, and 2 mm.

The sieves with the content were vibrated using a mechanical sieve shaker (Octagon Digital, Endecotts Limited, England) at 3,000 rpm, and an amplitude of 3.0 mm for fifteen minutes. The materials with particle sizes 1.18 mm, which conformed to the ASTM classification of medium sand, were chosen.

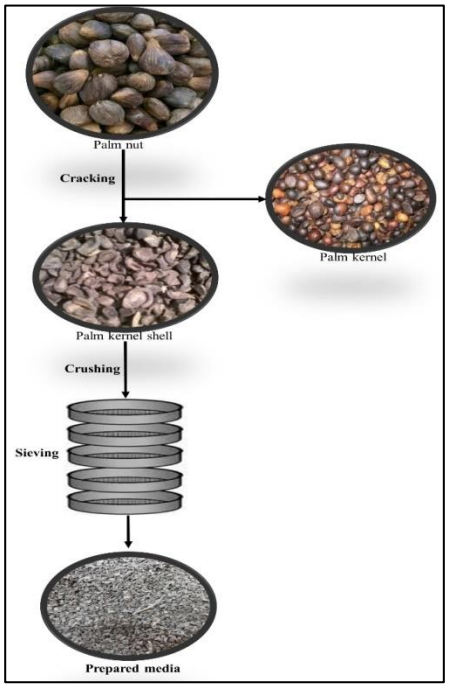


Fig. 1. Schematic diagram of PKS production process.

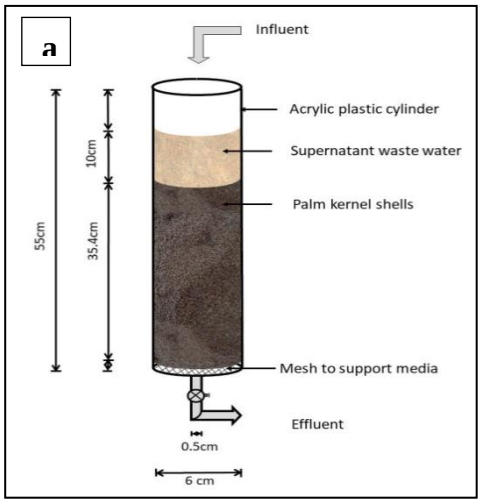
The small pycnometer method (BS 1377: Part 2: 1990) was used to determine the particle density. It was performed by dividing a 20 g sample by the effective volume, excluding pore space. Deionized water was added to the sample and gently boiled to eliminate air-filled pores and obtain the effective volume of the particles. The submerged particles were left to saturate for 24 h [28]. The particle density was evaluated using Eq. (1).

$$\rho_p = \frac{M_2 - M_1}{(M_4 - M_1) - (M_3 - M_2)} \quad (1)$$

Where ρ_p is the particle density, M_1 is the mass of pycnometer, M_2 is the mass of pycnometer and media, M_3 is the mass of pycnometer, media and deionized water and M_4 is the mass of pycnometer and deionized water.

C. Filtration Column Design and Characterisation

The experimental setup was designed as a batch system with a static bed. The setup consisted of acrylic plastic filter columns each having an internal diameter of 6cm and a height of 55 cm, as shown in Fig. 2. A small outlet of 0.5 cm diameter was made at the bottom to serve as a sampling point.



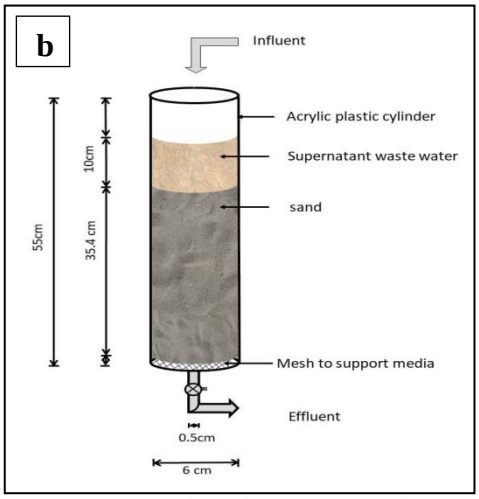


Fig. 2. Schematic diagram of PKS filter (a) and sand filter (b) used in clarified POME treatment study.

The filter materials were manually packed into the cylinder and levelled after every 10 cm by manual shaking. Each packed bed contained filter material of depth 35.4 cm (a working volume of 1000 mL). After packing, the bulk density and total porosity were determined. The analytical methods followed were based on those used by other researchers [28, 52, 54]. The dry weight of the filter media was divided by the volume occupied by the media (1000 mL) to obtain the bulk density. The porosity of the filter column was evaluated using (2).

$$p = \left(1 - \frac{\rho_B}{\rho_p}\right) \times 100 \quad (2)$$

Where *p* is the porosity in percentage of the effective volume, ρ_B is the bulk density and ρ_p the particle density.

D. Experimental Setup

At the start of the experiment, the outlet valves of the filter columns were closed. The filters were then fed with distilled water and allowed to stand for 24 h after which the outlet valves were opened and drained. The process was repeated after 24 h. Samples of the distilled water from the filters were taken for analysis to understand the possible contribution of the media to the test parameters. The influent POME was then fed from the top of each filter with the outlet valve closed. A constant-head reservoir was placed overhead the experimental set-ups and connected to the set-ups through a float valve to ensure that filtration occurred under constant-head conditions. Moreso, a minimum supernatant POME level of 10 cm was maintained over each media surface. These steps were taken to ensure steady-state and continuous anaerobic conditions within the filter columns. Effluent was drawn from the bottom of each filter column for analyses at 0-, 24-, 48-, 72-, 96-, and 120-h hydraulic retention times. Three replicate filter columns were used for each filter media, and the experiment was run in triplicates. The experiments were conducted at a room temperature of about 25 ^{o}C.

E. Laboratory Analysis

Laboratory analysis was performed on the influent POME as well as the effluent from each of the filter columns. The effluents from the filter columns were analysed at the start of the experiment and at 24-h intervals as previously reported. The colour and COD were analysed using the Hanna multiparameter photometer (HI83399) (Nusfalau, Romania) with associated reagents and methods of analysis. All analyses were performed in triplicates, and the mean values were taken. The efficiency of a filter media was based on the percentage reduction in the initial concentration of each parameter assessed using Eq. (3).

$$\text{Removal Efficiency (\%)} = \left(\frac{C_{in} - C_{out}}{C_{in}}\right) x100 \quad (3)$$

Where C_{in} and C_{out} represent the initial and final individual parameter concentration in mg/L.

F. Contaminant Removal Kinetic Modeling

The removal kinetics for COD and colour were determined using the uptake-time data obtained from the experimental results. Pollutant degradation was considered an irreversible reaction. The four kinetic models used by Yin *et al*. [55] were adopted. The kinetic models corresponding to zero-order (c–t), 1st-order (-lnc–t), 2nd-order (1/c–t) and 3rd-order ($1/c^2$–t) were plotted. The rate of zero-order kinetics is independent of the concentration of the contaminant. However, for 1st-, 2nd- and 3rd-order kinetics, the removal rates are dependent on the concentration of the contaminants [56]. The linear equations for the four kinetic models are as presented in Eq. (4) to (7).

$$\text{Zero} - \text{order: } [C] = -kt \quad (4)$$

$$1\text{st} - \text{order: } \ln[C] = -kt + \ln[C_0] \quad (5)$$

$$2\text{nd} - \text{order: } {}^{1}/_{[C]} = kt + {}^{1}/_{[C_0]} \quad (6)$$

$$3\text{rd} - \text{order: } {}^{1}/_{[C]^2} = kt + {}^{1}/_{[C_0]^2} \quad (7)$$

The best-fitting linear models for c–t, -lnc–t, 1/c–t and $1/c^2$–t for the pollutants were determined for the description of the pollutant removal mechanism. The correlation coefficient (R^2) values for the four kinetic models were compared. The model with the highest R^2 value was taken to be the best model for the overall reaction order.

G. Statistical Analysis

Statistical analysis was performed using SPSS statistical software (version 16). A test for normality was performed using the Shapiro-Wilk test with a significance level of 95%. The means and standard deviations were recorded for all the data. A t-test (α=0.05) was used to test for the significance of differences between the performances of the two filters.

III. Results and Discussion

A. Properties of Filter Media and Packed Bed

The properties of the filter media (PKS and sand) and packed bed are presented in Table II. For both filter media (PKS and sand), a particle size of 1.18 mm which conformed to the ASTM classification of medium sand were used. In a study, Liew *et al*. [35] used three different sizes (4.75–2.36 mm, 1.18–0.71 mm and 0.425–0.30 mm) of PKS activated

carbon as carrier material to remove COD from POME. They found that activated carbon with a size of 1.18-0.71 mm recorded the highest COD reduction. The particle size partly determines the bed porosity and has the potential to enhance the removal efficiency of COD and colour by the filters [57].

TABLE II: CHARACTERISTICS OF PKS AND SAND FILTERS

Parameter	PKS	Sand
Particle size (mm)	1.18	1.18
Particle density (kg/m^3)	1,330	2,220
Bulk density (kg/m^3)	676	1,560
Total Porosity (%)	49	30

The PKS filter had a higher bed porosity of 49% as against 30% for the sand bed filter. Sand is reported to have a typical porosity of 37–40% [58]. The porosity of the packed bed is strongly influenced by the particle shape, orientation, and size distribution [59]. PKS has a rough surface, which could increase the physical entrapment of organics in the POME. Moreover, PKS is more porous and may allow additional surface area or dead volume for contaminant removal. But sand has a smooth surface and is non-porous [60]. Filter bed porosity has a strong influence on head loss and filtration effectiveness. Small porosity leads to higher head loss and a reduced filtration rate over the operational period [61] but could produce an effluent of a better quality.

B. Characteristics of Influent Wastewater

The characteristics of the influent wastewater (Table III) and distilled water from the filters (Table IV) are presented. The mean influent wastewater COD concentration was 19947 (SD = 626) mg/L. The COD concentration in this study is higher than the COD of secondary POME from the final discharge pond reported by Darajeh *et al*. [62]. The COD is also higher than the greywater COD of 23–8071 mg/L [63], as well as those of wastewater from cheese whey, landfill leachate, and wineries but lower than the COD of wastewater from poultry slaughterhouses, diaries and olive oil mills [64]. The COD is also higher than biodigester effluent [65]. The colour ranged from 7117–8544 Pt-Co with a mean concentration of 8067 (SD = 823) Pt-Co. The colour of the wastewater is higher than that of wastewater from textile dye processing (50–2500 Pt-Co) [66] and POME from the final discharge ponds (2707 Pt-Co) [67], but lower than that of POME from anaerobic ponds (54200 Pt-Co) [68] and olive oil mill wastewater (19750 Pt-Co) [69]. The colour and COD indicate the presence of dissolved organic and inorganic matter in the wastewater.

The characteristics of distilled water after 24-h contact with the filter media were lower for the sand filter than for the PKS filter. Sand only impacted the colour of the water, increasing the colour by 190 Pt-Co with no contribution to COD. PKS rather impacted highly on the colour (883 Pt-Co) and COD (488 mg/L) of the distilled water. The results presuppose that the filter media used in this study were potential contributors to the parameters measured and could lead to spikes in the initial concentrations of the test parameters.

TABLE III: CHARACTERISTICS OF RAW AND INFLUENT POME

	Colour	COD	TS	SS	Total nitrogen	Phosphorus	Potassium
Fresh POME	16,180 (1,261)	56,357 (3,441)	3,976 (1,397)	3,618 (1,551)	246 (86)	49 (24)	156 (24)
Influent POME	8,067 (823)	19,947 (626)	20.3 (2.1)	9.7 (1.3)	200 (28.4)	60 (7.2)	193 (18.0)

Values are Mean (Standard Deviation); Colour is in Pt-Co; All other parameters are in mg/L

TABLE IV: CHARACTERISTICS OF DISTILLED WATER FROM PKS AND SAND FILTERS

Parameter	Mean (Standard Deviation)	
	PKS filter	Sand filter
Colour (Pt-Co)	883 (63.2)	190 (13.9)
COD (mg/L)	488 (30.4)	0

TABLE V: MEAN CHARACTERISTICS OF INFLUENT AND EFFLUENT WASTEWATER AFTER 120-HR RETENTION TIME

Parameter	Mean (Standard Deviation)			p-value[1]	p-value[2]	p-value[3]	GEDS
	Influent	PKS	Sand				
Colour (Pt-Co)	8,067 (823)	2480 (126)	3040 (164)	<0.001	<0.001	0.087	300
COD (mg/L)	19,947 (626)	4560 (158)	4090 (142)	<0.001	<0.001	0.492	250

GEDS – Ghana Effluent Discharge Standard [70]

p-value[1] = Statistical significance between influent and effluent from PKS filter.

p-value[2] = Statistical significance between influent and effluent from sand filter.

p-value[3] = Statistical significance between effluent from PKS and sand filters.

C. Mean Characteristics of Final Effluent from Filter Columns

The mean characteristics of the influent wastewater and effluent from the filters after 120-hr retention time are presented in Table V. There were differences in the performances of different media types in removing specific pollutants in the wastewater.

At the end of the experimental period, both filter media were able to reduce the concentrations of COD and the colour of the influent wastewater. There were differences in the characteristics of the final effluent between the filter media types. The concentration of COD was lower for the effluent from the sand filter than for PKS filters. On the other hand, the colour was lower for the PKS filter (2480 Pt-Co) than the sand filter (3040 Pt-Co). The removal efficiency of the respective media is determined by the particle size, bed porosity, and flow rate [57, 71]. In granular bed filtration, physical and biological processes are utilized. The biological mechanism works concurrently with the physical interactions [60]. This takes place at the upper layer of the filter and within the filter bed, where organics have been trapped. Biological activities include predation, elimination, natural inactivation, and partial reduction of organic carbon due to microbial metabolism [72]. Physical processes are controlled

by the structure and packing of the porous material and occur throughout the entire bed depth.

The physical interactions include sedimentation, interception, and straining of solid particles in the pores of the filter bed [71]. The combined effect of biological and physical processes could have led to the COD and colour removal by the filters.

For the PKS and sand filters used in the current study, a paired-sample t-test showed a statistically significant difference in the mean characteristics between the influent and effluent wastewater at 1% level. The results suggest that the PKS and sand filters were able to treat the wastewater. However, the mean characteristics of the final effluent from both filters compared with the Ghana Effluent Discharge Standard (GEDS) (see Table V) show that the wastewater does not meet the standard to be discharged into the environment. The concentration of the final effluents after a 120-hr retention time was higher than the GEDS limits by 8–18 times for PKS filters and 2.5–16 times for sand filters. The remarkable performance of sand in treating wastewater at low organic loading rates has been reported in previous studies [26, 28, 73]. The high concentrations of the influent wastewater COD and colour may have contributed to the filters' inability to reduce the contaminant levels within discharge limits. Conventionally, treatment of industrial wastewater is mostly preceded by a pre-treatment step. To reduce the concentration of the influent COD and colour, anaerobic digestion in closed bioreactor could be used. In addition to reducing the organic loadings, anaerobic digestion of POME could generate biogas, a green and clean energy, for use in the production process [74].

D. Pollutant Removal Efficiency

1) Colour reduction

The trend of colour removal efficiency in the PKS and sand filters over the experimental period is presented in Fig. 3. The effluent from both filters immediately after the addition of influent POME showed a spike in colour. The percentage increase was 7% for PKS and 1% for sand. The spike in colour may have been contributed by the media themselves, as seen in Table IV.

But after 24-h contact time, there were reductions in the colour for both media, with a higher reduction of 27% recorded by the PKS. The sand filter was able to reduce the colour by 7% within the 24-h retention time. PKS is reported to be porous, which could allow better adsorption of suspended and dissolved organics, which are responsible for the colour of POME. This may have contributed to the increased initial colour removal of 27% compared to the sand filter.

However, when the adsorptive surfaces are used up, the rate of contaminant removal declines. For the PKS filter, about 61% of the colour was removed within 72 h, whiles the remaining 8% was achieved within 48 h. The efficiencies of the media types in reducing colour at the end of the experimental period were in the order PKS (69%) > sand (62%). Alkhatib *et al.* [37] investigated the removal of residual colour from treated POME using PKS as an adsorbent. Under ideal conditions, the process removed 89.95% of residual colour. The colour removal was found to increase with an increase in contact time and adsorbent dosage but decreased with an increase in pH. Jalani *et al.* [38] carried out an adsorption study using steam-activated PKS as an adsorbent to remove colour from POME and achieved a maximum colour removal of 76% within 72 h. Activated carbon from PKS was used to remove over 90% of the equilibrium adsorptions for colour (methylene blue) after a 4-h contact time [36].

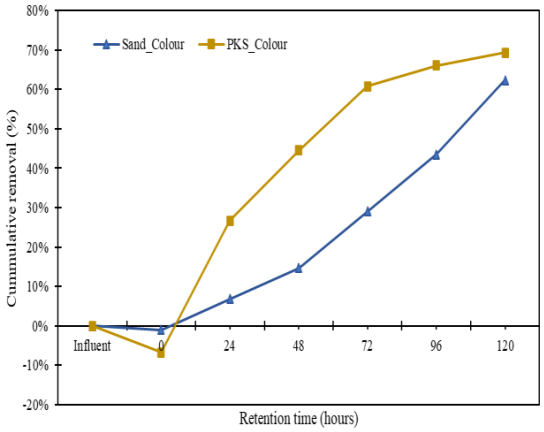


Fig. 3. Colour reduction efficiency for PKS and sand filters.

The colour removals reported by previous studies were 10–30% higher than those obtained in the current study. The differences in the removal rate between the previous and current studies may be due to the properties of the media and the concentration of the influent wastewater. The filter media used in the previous studies were all activated carbon produced from PKS. Activated carbon is reported to possess a large volume of micropores and a large specific surface area [75], and this may have accounted for the higher colour removal. In addition, the colour of the influent wastewater in the current study was higher than that used in the other previous studies. For instance, the initial colour of the POME samples used by Jalani *et al.* [38] was 3500–6500 Pt-Co. That notwithstanding, the difference in the mean colour concentration between PKS and sand filters at the end of the experimental period in the current study was not statistically significant (p=0.087). This signifies that the removal efficiencies of the PKS and sand filters were comparable.

2) COD reduction

In Fig. 4, the trend of COD removal efficiency is shown for PKS and sand filters.

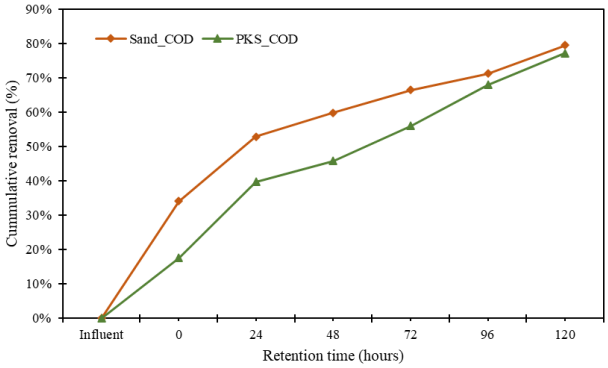


Fig. 4. COD removal efficiency for PKS and sand filters.

The sand filter was characterised by a higher initial COD reduction compared to the PKS filter. An initial COD

reduction of 34% for the sand filter as compared to 18% for the PKS filter was recorded. Subsequently, each of the filters recorded increased performance in COD reduction, but at varying rates. The COD reductions for the sand and PKS at the end of the experimental period were 79% and 77%, respectively. Dalahmeh *et al*. [28] observed a similar trend in greywater COD reduction of 72% for sand, but at a much longer contact time of 113 days.

Other studies have reported 83–90% COD removal rates at different hydraulic loading rates in anaerobic sand filters [76]. The reduction of COD of 79% by the sand filter was higher in this study than the 58% reported by Kätzl *et al*. [73]. The removal of COD may have occurred through straining and accumulation of organics in the packed bed and microbial degradation of organics [77]. However, it has been reported that an increase in contaminant concentration usually increases the adsorption capacity of the media up to the point when the active adsorption sites are saturated [39]. The high concentration of influent COD could have led to the high initial COD reduction that was measured. Even though the COD removal efficiency for sand filters was better than that for PKS filters, the difference in the mean COD concentrations at the end of the 120-hr retention time was not statistically significant ($p = 0.492$). The removal efficiency of COD is reported to increase with an increase in the concentration of contaminants in influent wastewater because of the greater availability of dissolved and suspended solids to be retained in the packed filter bed [76].

E. Kinetic Models for COD and Colour Removal

The fitting curves for COD and colour removal in the PKS and sand filters were determined from the experimental data. The fitting curves for zero-, 1st-, 2nd-, and 3rd-order COD and colour removal in the PKS filters are presented in Fig. 5 and Fig. 6, respectively. Similarly, the fitting equations for the COD and colour removal in the sand filters are presented in Table VI. The correlation coefficient, R^2 ranged from 0.7295 to 0.9866. However, the R^2 values corresponding to the best -fitting curves ranged between 0.9719 and 0.9866.

For the PKS filter, the best-fitting curves for COD and colour removal followed the first- and second-order kinetics, respectively. This implies that the COD and colour removal rates are dependent on the concentrations of COD and colour in the solution. For such concentration-dependent kinetics, the rate of reduction will decrease gradually as the concentrations of the contaminant decrease [61]. In effect, the removal efficiency of PKS filters for COD and colour will decline as the contaminants decrease. When considering the sand filter, the best-fitting curves for COD removal followed the first-order kinetics, but those for colour removal followed the zero-order kinetics. Thus, the rate of colour removal by the sand filter is independent of the concentration. The kinetic equations for the PKS filter were used to forecast the retention time that would be required to bring the pollutant levels below the GEDS (see Fig. 7).

An estimated retention time of 17 days, 18h, and 41 m is required to reduce the COD to 250 mg/L. Similarly, to reduce the colour of the wastewater below the allowable limits of 300 Pt-Co, an estimated retention time of 44 days, 54 h, and 27 m is required. The estimated retention time is an indication of the high concentration of the target pollutants in the POME.

The margin of deviation of R^2 values from unity indicates the level of irreconcilability of each kinetic model [78]. The values of the reaction rate constant were generally low. The relatively low reaction rate constant of the selected kinetic models could have triggered the slow pollutant removal rates as noted also by Yin *et al*. [55]. On the other hand, the high concentration of influent pollutants could possibly have led to the lower rate constant compared to the findings of other studies, as observed by Shen *et al*. [79]. The rate of adsorption may be limited by external and internal/intra-particle diffusion and bulk solution transport [80].

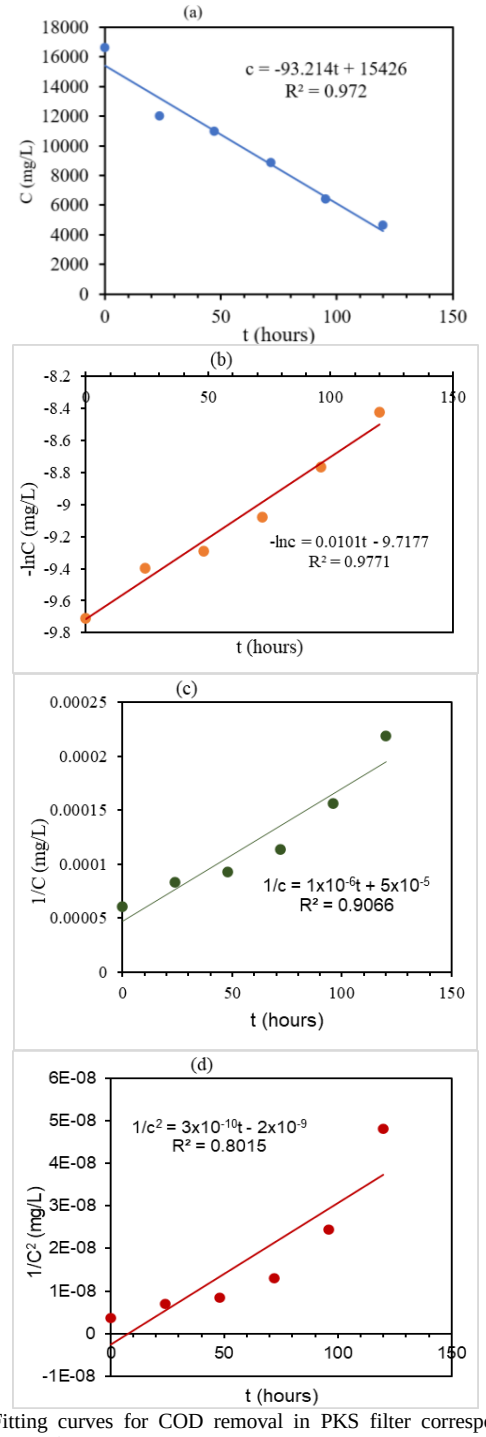


Fig. 5. Fitting curves for COD removal in PKS filter corresponding to zero-order (a), first-order (b), second-order (c), and third-order (d) kinetic models.

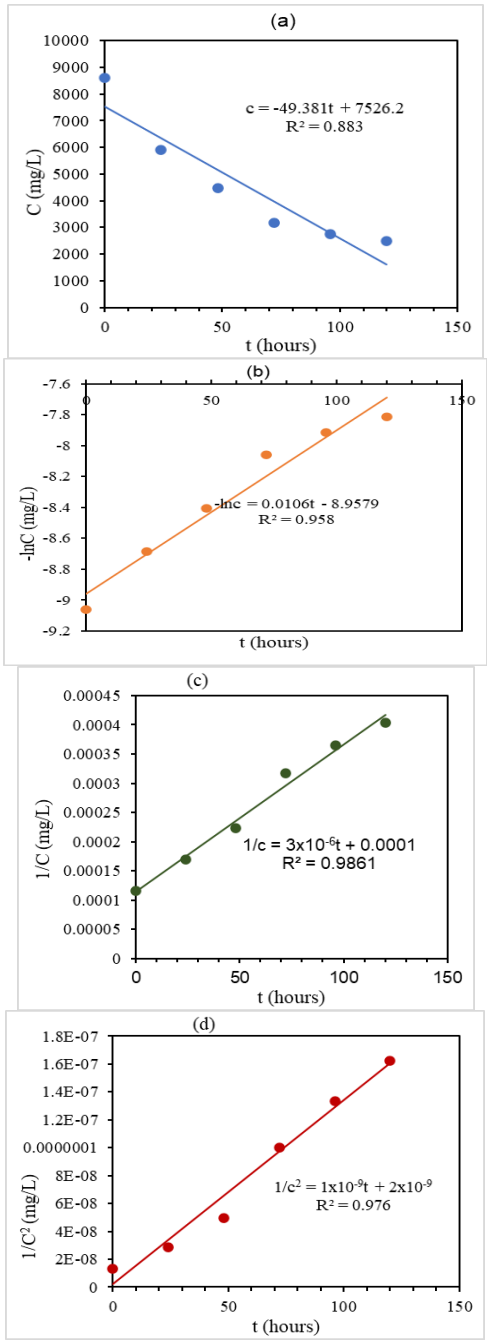


Fig. 6. Fitting curves for colour removal in PKS filter corresponding to zero-order (a), first-order (b), second-order (c), and third-order (d) kinetic models.

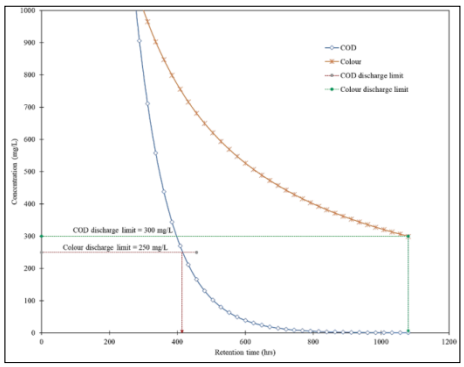


Fig. 7. The estimated retention time to reduce pollutants below allowable limits for discharge in Ghana.

The smaller particle size of the media (1.18 mm) used in this study might have contributed to deviations in the kinetic models [78]. Large particle sizes have been identified as possessing a large internal surface area which enhances sorbate diffusion into the internal sites of the adsorbent [81]. The effectiveness of the model obtained to describe and approximate the removal kinetics could be affected by the presence of high-affinity pollutants in the effluent [78]. The correlation between the experimental results and the predicted results from the selected kinetic equations are plotted in Fig. 8.

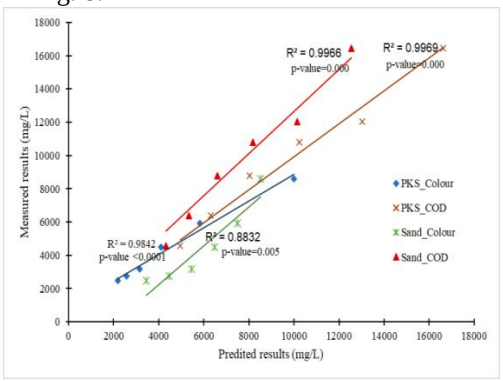


Fig. 8. Correlation between experimental results and predicted results from kinetic equations.

TABLE VI: FITTING EQUATIONS FOR COD AND COLOUR REMOVAL IN SAND FILTER

Models		COD	Colour
Zero-order	Equation	c=−68.679t + 11972	c= -42.369t + 8520.5
	R^2	0.9397	**0.9719**
1st-order	Equation	-lnc=0.0089t – 9.4369	-lnc=0.0079t – 9.1166
	R^2	**0.9801**	0.9131
2nd-order	Equation	$1/c=1x10^{-6}t + 7x10^{-5}$	$1/c=2x10^{-6}t + 9x10^{-5}$
	R^2	0.9397	0.8258
3rd-order	Equation	$1/c^2=4x10^{-10}t + 3x10^{-10}$	$1/c^2=7x10^{-10}t – 3x10^{-10}$
	R^2	0.8440	0.7295

The R^2 values in bold indicate the selected kinetic models.

The correlation coefficients ranged from 0.8832 (p = 0.005) for colour removal in the sand filter to 0.9969 (p = 0.000) for COD removal in the PKS filter. This shows a strong correlation between the experimental results and the predicted results. The experimental results agree very well with the predicted results, and therefore the kinetic equations could be used to predict COD and colour removal from clarified POME in a PKS granular filter column.

IV. CONCLUSIONS

This study assessed the potential of using PKS as a granular filter media for treating clarified palm oil mill effluent. PKS filter performance was comparable to the

reference filter (sand) for the removal of colour and COD. The removal efficiency for the PKS filter was 77% for COD and 69% for colour. Similarly, the performance of the reference filter media (sand) for COD and colour was, respectively, 79% and 62%. Comparing the performance of the PKS filter with that of the sand filter, the differences were not statistically significant. Removal of COD and colour using PKS and sand filters could be described and approximated using different kinetic models (R^2=0.9719 – 0.9866). The rate of COD removal was consistent with first-order kinetics for both PKS and sand filters, implying its dependence on the instantaneous COD concentration. However, colour removal in PKS and sand filters followed second- and zero-order kinetics, respectively. Thus, the rate of colour removal in the sand filter is independent of the instantaneous colour concentration. The removal of specific pollutants using the selected kinetics models agreed well with the experimental data. The proportions of the pollutants removed by the PKS filter considerably minimise the negative effect of the discharge of the influent POME into the environment. However, filters were unable to reduce the influent concentration of colour and COD below the acceptable limit for discharge into the environment. To enhance the chances of bringing the COD and colour concentrations in the effluent within the allowable limits, low-cost treatment methods such as anaerobic digestion of POME could be applied prior to the application of the PKS filtration system. Such a technology could generate biogas, which could be used as a fuel source at the processing mills as well as reduce the concentration of pollutants in the POME. PKS granular filter media may be more useful in treating wastewater with low pollutant loading rates. Studies should be conducted to determine the number of times that non-activated PKS filter media can be used before replacement. Further laboratory-scale studies on clarified palm oil mill wastewater using PKS as granular media may be conducted to verify the estimated retention times of 18 days for COD and 45 days for colour. In addition, the experiment should be repeated using activated PKS granular filter media.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

Eric Awere: Conceptualization, Methodology, Investigation, Data Curation, Data Analysis, Writing – Original Draft. Peter Appiah Obeng: Conceptualization, Methodology, Validation, Data Analysis, Writing – Review & Editing, Supervision. Alessandra Bonoli: Conceptualization, Methodology, Resources, Writing – Review & Editing, Supervision.

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