Removal of ammonia nitrogen, nitrate, phosphorus and COD from sewage wastewater using palm oil boiler ash composite adsorbent

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ABSTRACT

Sewage treatments are introduced in the country to protect the health of human and environment. In this study, palm oil fuel ash (POFA) was explored as an adsorbent media for the treatment of a sewage wastewater. The optimum shaking speed, shaking time, pH, and dosage for chemical oxygen demand (COD), ammonia nitrogen, nitrate and phosphorus removal were investigated using the adsorbent media of particle sizes ranging from 2.00 to 3.15 mm. POFA and composite POFA chemical composition and characteristics were then determined. Results indicated that sewage concentrations of COD (63.39 mg L⁻¹), ammonia nitrogen (6.01 mg L⁻¹), nitrate (0.63 mg L⁻¹) and phosphorus (0.43 mg L⁻¹). The optimum conditions for shaking were determined at 200 rpm according to the adsorption of COD, ammonia nitrogen, nitrate and phosphorus by the media. Optimum shaking time of 20 min for ammonia nitrogen, nitrate phosphorus and COD optimum shaking time is 30 min. The optimum pH value for COD, nitrate and phosphorus removal using composite POFA was obtained at pH 6 and for ammonia nitrogen is pH 9. Microstructures of the prepared composite POFA were analyzed using Brunauer–Emmett–Teller, scanning electron microscope, X-ray diffractometer and X-ray fluorescence measurements. These results suggest that composite POFA can be used as a potential effective, low cost and eco-friendly green adsorbent for the removal of COD, ammonia nitrogen, nitrate and phosphorus from sewage wastewater.

Keywords: Palm oil fuel ash (POFA); Adsorption; Physico-chemical analysis; Microstructure; Element analysis

1. Introduction

Water is important for living matters such as living consumption, industries and agricultural uses [1,2]. However the source of drinking water was polluted by (1) organic contaminants such as chemical oxygen demand (COD), total organic carbon; (2) inorganic contaminants such as ammonia, nitrite, nitrate, phosphorus, sulphur and heavy metals. These contaminants cause severe impact to the environment and living organisms if their concentrations in drinking water exceed concentration regulated limits [3].

Malaysia is a tropical country rich in water resources. However, many of the water resources are polluted. A recent study has revealed that 15 out of 56 lakes assessed are eutrophic [4]. To achieve developed nation status by the year 2020, Malaysia has experienced rapid development in terms of urbanization, industrialization, tourism and communications [5]. Nevertheless, these activities have resulted in an increase in water pollution around the regions of the country [6,7] hence limiting the availability of freshwater supplies. The concentration of ammonia nitrogen (NH₃–N) in water-bodies must not exceed the Malaysian regulated limit of 1.5 ppm in water intake points of drinking water treatment.
palm [8]. Hence, nitrogen removal from sewage before discharge to environment is important to preserve cleanliness of waterbodies. The discharge limit of ammonia nitrogen (NH$_3$–N) from sewage treatment plants (STPs) in Malaysia is stated in Environmental Quality (Sewage) Regulation 2009. Consequently, many of the STPs have combined anoxic tank together with extended aeration process for nitrogen removal process.

Palm oil is a popular vegetable oil for cooking and food processing [9]. Currently, major world producers of palm oil are Indonesia, Malaysia, Thailand, Colombia and Nigeria. Indonesia is the world's first major producer and exporter of palm oil followed by Malaysia [10]. The Malaysian oil palm plantation has increased from 5.74 million ha in 2016 to 5.81 million ha in 2017 [11]. As a result of the global demand on oil palm, the growth of the oil palm industry generates an average of 53 million tonnes of non-toxic biomass annually [12]. It was reported that, estimated 4 kg of dry biomass were produced with every 1 kg of palm oil production. After the fresh fruit bunch being processed in the palm oil mill, the milling stage produces about 22% empty fruit bunches (EFB), 9% shells, 14% fibers, 60% of palm oil mill effluent, 5% palm kernel seeds and 20% crude palm oil [13]. Meanwhile it has been reported that, 100 million dry tonnes of palm oil solid biomass would be generated by the year 2020 from the 80 million tonnes of dry oil palm biomass generated in 2010 and will continue to rise due to the expected expansion of crop plantations occasioned by the high global demand for palm oil [14,15]. Palm oil fuel ash (POFA) is one such waste, a recycled material that originated from the palm oil industry.

POFA is the ash that is produced in the plant boiler by burning the oil palm shell and EFB as a fuel and burnt at 800°C–1,000°C [16]. It was reported that 4 million tonnes of this POFA are generated annually which is expected to increase due to increasing global demand for palm oil [17]. Currently, POFA usage is very limited and unmanageable, and most of it was disposed of in landfills. Consequently, it has caused numerous environmental problems [18]. The infiltration of POFA into the groundwater tables and aquifer systems if not curtailed poses serious challenges and potential health hazards to the public and the environment [19]. The management of these wastes through recycling has been of paramount interest of researchers. POFA chemical composition varies with average of 60% silica and 7% carbon depending on manufacturing conditions [20,21]. However, the application of oil palm biomass as commercialized adsorbents is still in research stage. In order to enhance the value of this material, POFA could be developed into a natural low-cost absorbent for the removal of heavy metals in the industrial wastewater. On top of that, the abundant and cheap supply of the biomass materials will further justify its use in the wastewater industry [22–25]. In addition, the abundant and cheap supply of the biomass materials will further bring justification to its usage. Many different wastewater treatment technologies are available, including conventional methods such as chemical precipitation, coagulation, reverse osmosis, ion exchange, membrane filtration, oxidation, air stripping, sedimentation and adsorption [22,26–29].

Adsorption has been proposed as a promising technique for the removal of diverse contaminants, as it is simple, easy to operate, and highly effective in removing heavy metals from effluents with either high solute loadings or dilute concentrations [28–30]. However, the application of oil palm biomass as commercialized adsorbents is still in research stage. The main objective of this study is to investigate the performance and characteristics of composite POFA developed as a natural low-cost adsorbent for removal of COD, ammonia nitrogen, nitrate and phosphorus from sewage wastewater. Additionally, the adsorption mechanism as well as physicochemical analyses was conducted in the present study. Batch adsorption experiments were conducted to further investigate the composite POFA under varying experimental conditions, such as effect of shaking speed, effect of contact time, effect of solution pH, effect of adsorbent dosage and effect of composite POFA particle size.

2. Methodology

Samples of wastewater were collected from sewage treatment plant, Bukit Puteri, Universiti Kebangsaan Malaysia, Bangi. All samples were stored at 4°C for further study. The POFA was taken from the middle of the flue tower and was collected from Sime Darby, Port Dickson, Negeri Sembilan. POFA was sieved through with sieve size diameter between 75 and 250 μm. It was washed with deionized water for several specific times to remove foreign particles, immediately stored at oven for dry at 105°C over night. The adsorption media POFA (700 g) with particles size less than 250 μm was blended with ordinary portland cement 300 g that was used as a binder into ratio 7:3 composition matter, and about 60%–70% by media weight of distilled water was added. It was allowed to harden for 72 h and then submerged in water for a curing period of 96 h. The composite POFA media were then crushed using mortar and pestle, then sieved to obtain the desired particle size 2.00–3.15 mm [31].

In this experiment, ammonia, nitrate and phosphorus concentrations were measured by using a Hach’s DR2010 spectrophotometer at 425, 353 and 535 nm wavelengths, respectively. Ammonia was measured by Nessler Method (Method: 8038). Nitrate was measured by Cadmium Reduction Method (Method: 8171), whereas phosphorus was measured by PhosVer 3 Method (Method: 8048) [32]. In addition, reactor digestion closed reflux colorimetric method for low range determination was used to determine COD concentration.

2.1. Removal efficiency and adsorption capacity

The adsorption study was performed using 5 g of media, 200 rpm, 60 min, pH 6 and 100 mL raw sewage wastewater and 50 g L$^{-1}$ of media concentration at an optimum condition described in the previous study [33]. Adsorption isotherm tests were the reaction mixture consisting of a 100 mL raw sewage wastewater solution with varying adsorbent dosage, shaking speed, contact time and pH. Percentage of removal for COD, ammonia nitrogen, nitrate and phosphorus were obtained using the following formula:
POFA, and is listed in Table 1. The POFA composition exhibited in raw materials POFA and composite POFA (Malaysia) was used to determine the percentage of chemical sewage wastewater, respectively. The initial value of each selected parameter was 63.39 mg L–1 for COD, 6.01 mg L–1 for ammonia nitrogen, 0.63 mg L–1 for nitrate, and 0.43 mg L–1 for phosphorus.

2.2. Characterization of composite POFA

Field emission scanning electron microscope (SUPRA 55VP, Zeiss, Germany) was used to characterize the morphology of composite POFA. Surface area and pore volume were calculated by single-point Brunauer–Emmett–Teller (BET) method and analyzed using (ASAP 2010, Micromeritics, America) to indicate the composite POFA as an efficient adsorbent. The crystallinity of the composite POFA was determined using X-ray diffractometer (XRD) recorded on a Advance D8 QUEST X-ray powder diffractometer (Bruker) in the range of 2θ = 2°–90°, with Cu Kα (λ = 1.5418 Å) radiation. The X-ray fluorescence spectrum analysis (Bruker S8-Tiger, Malaysia) was used to determine the percentage of chemical composition present in raw materials POFA and composite POFA, and is listed in Table 1. The POFA composition exhibits a rich content of silicon dioxide (SiO₂) compound, calcium oxide (CaO) and potassium oxide (K₂O) and was similarly reported in the previous studies [34,35].

### Table 1

| POFA composition    | Percentage (wt.% | Composite POFA composition | Percentage (wt.%)
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>SiO₂</td>
<td>46.35%</td>
<td>CaO</td>
<td>30.65%</td>
</tr>
<tr>
<td>CaO</td>
<td>7.94%</td>
<td>SiO₂</td>
<td>27.88%</td>
</tr>
<tr>
<td>K₂O</td>
<td>6.38%</td>
<td>Fe₂O₃</td>
<td>4.64%</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>5.27%</td>
<td>Al₂O₃</td>
<td>4.19%</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5.22%</td>
<td>K₂O</td>
<td>3.68%</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>3.78%</td>
<td>SO₃</td>
<td>1.84%</td>
</tr>
<tr>
<td>MgO</td>
<td>3.26%</td>
<td>MgO</td>
<td>1.60%</td>
</tr>
<tr>
<td>SO₄</td>
<td>0.81%</td>
<td>P₂O₅</td>
<td>1.59%</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.60%</td>
<td>TiO₂</td>
<td>0.49%</td>
</tr>
<tr>
<td>Cl</td>
<td>0.25%</td>
<td>Cl</td>
<td>0.15%</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.16%</td>
<td>Na₂O</td>
<td>0.14%</td>
</tr>
<tr>
<td>MnO</td>
<td>0.09%</td>
<td>MnO</td>
<td>0.11%</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>0.08%</td>
<td>ZrO₂</td>
<td>0.07%</td>
</tr>
<tr>
<td>CuO</td>
<td>0.04%</td>
<td>CuO</td>
<td>0.03%</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.02%</td>
<td>ZnO</td>
<td>0.01%</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.02%</td>
<td>Cr₂O₃</td>
<td>0.01%</td>
</tr>
<tr>
<td>SrO</td>
<td>0.01%</td>
<td>NiO</td>
<td>57 PPM</td>
</tr>
<tr>
<td>Rb₂O</td>
<td>85 PPM</td>
<td>Rb₂O</td>
<td>57 PPM</td>
</tr>
<tr>
<td>Nb₂O₅</td>
<td>25 PPM</td>
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The ammonia nitrogen, nitrate and phosphorus removals were nearly the same from shaking time of about 20 min. The removal of COD was increasing with the increase in time and attained equilibrium in about 30 min. This phenomenon at the early stages is attributed to the vacant sorption sites on the media that initially became increasingly abundant and then slowed down owing to increasing competition for available vacant sites as a result of adsorbate saturation on the adsorbent and repulsion between similarly charged species. The plot exhibited a single, even and continuous profile, suggesting the likelihood of monolayer coverage on the surface of the adsorbent. Similar sorption traits have been reported in the literature [37,38]. The shaking time of 20 min was adopted, which obtained ammonia nitrogen 43%, nitrate 100% and phosphorus 100% removal rates and COD optimum shaking time 30 min with 99% removal rate.

\[
\text{Removal (\%)} = \left( \frac{(C_i - C_f)}{C_i} \right) \times 100
\]

where the initial (\(C_i\)) and final concentrations (\(C_f\)) for each parameter COD, ammonia nitrogen, nitrate and phosphorus may have attained equilibrium at 200 rpm (100%) for COD, nitrate and phosphorus such that no further improvement can be attained. This result may be attributed to the diffusion of the adsorbate in the liquid bulk to the adsorbent surface, which increased with the increase in shaking rate. Another reason may be due to the fact that the initial kinetic energy of the adsorbents and that of the sewage molecules increase as the shaking speed increases. Consequently, the probability of interaction between the molecules and adsorbent becomes significant; hence, the amount of adsorbate increases until it reaches the equilibrium state. After reaching equilibrium, the adsorption diminishes even with the increasing shaking speed. Thus, the condition after equilibrium is possibly caused by the extremely high kinetic energy of the molecules and adsorbent particles that limited their interaction with each other [36]. Hence, 200 rpm was selected for further study.

### 3.2. Determination of optimum shaking time

The concentration of adsorbate and the interaction time between the adsorbent and adsorbate play dominant roles in minimizing pollutants from sewage wastewater. The time duration needed to achieve maximum removal efficiency is the time when the sorption system attains equilibrium. Fig. 2 shows the effect of shaking time on COD, ammonia nitrogen, nitrate and phosphorus removal by the adsorbent. The ammonia nitrogen, nitrate and phosphorus removals in the sample after shaking at 50, 100, 150, 200, 250 and 300 rpm in an orbital shaker are shown in Fig. 1. The optimum removal for COD, ammonia nitrogen, nitrate and phosphorus by the adsorbent occurs at 200 rpm. At the beginning, the adsorption increases simultaneously with the agitation speed. After reaching 200 rpm, the adsorption dissipates even with a further increase in the shaking speed. Therefore, the adsorption may have attained equilibrium at 200 rpm (100%) for COD, nitrate and phosphorus such that no further improvement can be attained. This result may be attributed to the diffusion of the adsorbate in the liquid bulk to the adsorbent surface, which increased with the increase in shaking rate. Another reason may be due to the fact that the initial kinetic energy of the adsorbents and that of the sewage molecules increase as the shaking speed increases. Consequently, the probability of interaction between the molecules and adsorbent becomes significant; hence, the amount of adsorbate increases until it reaches the equilibrium state. After reaching equilibrium, the adsorption diminishes even with the increasing shaking speed. Thus, the condition after equilibrium is possibly caused by the extremely high kinetic energy of the molecules and adsorbent particles that limited their interaction with each other [36]. Hence, 200 rpm was selected for further study.

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3.3. Determination of optimum pH

Percentage of removal rate in the sample after the pH is adjusted from 4 to 10 and at an agitating speed of 200 rpm is shown in Fig. 3. A gradual increase is evident in the percentage uptake by the adsorbent up to pH 6 (100%) for COD, nitrate and phosphorus, and the uptake decreases from pH 7 to 10. For ammonia nitrogen, the percentage uptake by the adsorbent up to pH 9 (76%) is given in Fig. 3. When the pH increases in the solution, the number of negatively charged sites increases, whereas that of the positively charged sites decreases, thereby resulting in an electrostatic attraction between the charged particles. The uptake process increases until it reaches equilibrium. The decrease in the uptake with an increase in pH may be caused by the dissociation that occurs at the solid to liquid boundary because of the acid and base interaction [39]. The optimum pH condition for the COD, nitrate and phosphorus removal is at pH 6 and for ammonia nitrogen is at pH 9. This behaviour may be ascribed to the electrostatic attraction occurring between the solid adsorbent on which the ionizable surface groups presented a positive charge because of acidic condition and that of the organic functional groups of the adsorbate in the bulk liquid.

3.4. Determination of optimum dosage

Use of inadequate or excessive composite POFA may result in inadequate capacity in removal of parameters. Therefore, the optimum dose of the POFA must be determined to achieve economic savings and improve efficiency. The effect of the adsorbent dosage on adsorption was evaluated with an agitation speed of 200 rpm, a pH of 6, and an adsorbent mass ranging from 3 to 23 g. From the beginning,
the percentage removal increases with the increase in the adsorbent dose until it reaches an optimum mass of 8 g COD (65%), ammonia nitrogen (63%), nitrate (100%) and phosphorus (97%); then, the percentage removal begins to decrease with a further increase of the adsorbent dose as shown in Fig. 4. This behaviour can be explained considering that when the amount of adsorbent increases, the amount of available adsorption sites increases until the optimum mass is reached; any further increase in the adsorbent dose may result in aggregation, which can decrease the probability of molecules contacting all available adsorption sites [40].

3.5. Composite POFA characteristics

In general, all fly ash has the same fundamental chemical elements, but only in varying proportions [41]. Research highlights that oil palm ash evidently contains high level of alumina, calcium, potassium and silica that could be utilized...
to synthesize active compounds [42,43]. In this study, the results derived from the single-point BET analysis have shown that the specific surface area of composite POFA was found to be 48.6773 m$^2$ g$^{-1}$. Meanwhile, the results from the Barrett-Joyner-Halenda pore size distribution adsorption analysis for the total surface area and pore volume of POFA were to be 20.040 m$^2$ g$^{-1}$ and 0.090804 cm$^3$ g$^{-1}$, respectively.

Scanning electron microscope (SEM) was applied to observe the morphology and pore size of composite POFA as shown in Fig. 5. The surface is smooth and distributed with small pores. Some particles are scattered on the surface due to the remaining COD, ammonia nitrogen, nitrate and phosphorus on the composite POFA. Wang et al. [28] reported that adsorption process and capacity are closely linked with physical and chemical characteristics of the adsorbent such as particles size, pore diameter, quantity, specific surface area and surface chemical characteristics.

The mineral compositions of the composite POFA were detected via Bruker D8 Advanced XRD. Major mineral contents picked by the instrument were then identified using ICDD 2006 mineral identification approach, shown in Fig. 6. It can be seen that the peaks of the XRD diffraction indicate there were silica as calcium silicate ($\text{Ca}_2\text{SiO}_4 = 54.1\%$) and quartz ($\text{SiO}_2 = 45.9\%$). Crystalline cristobalite and silica in tridymite form are present [44], indicated by sharp spikes at $26^\circ \approx 27^\circ$ and $26.6^\circ$. Additionally, lower spikes at nearly at $20^\circ \approx 21^\circ$ and $20.8^\circ$ represent the quartz structure ascribing to the respective. Meanwhile, calcium silicate support establishes distinctive diffraction spikes at $29^\circ \approx 30^\circ = 29.5^\circ$.

![Fig. 5. Composite POFA before adsorption (a) and after adsorption (b).](image)

![Fig. 6. XRD pattern of composite POFA.](image)
4. Conclusion

The continuous rise in the waste generation from the oil palm mills activities has been the source of concern to researcher on the conversion of these huge waste to valuable product [45,46]. This current work has sheds light on several batch adsorption experiments for the removal of COD, ammonia nitrogen, nitrate and phosphorus from sewage that have been carried out using composite POFA as a natural low-cost adsorbent. The ability of the composite POFA adsorbent to minimize COD, ammonia nitrogen, nitrate and phosphorus from sewage wastewater was investigated. The results have clearly shown that the adsorption rate of COD, ammonia nitrogen, nitrate and phosphorus was initially very rapid in the first shaking speed of 200 rpm and in which period already 100% of total COD, nitrate and phosphorus was removed and 41% of ammonia nitrogen. Meanwhile, the adsorption capacity had increased slowly corresponding to contact time before arriving at a plateau value after 20 min of ammonia nitrogen, nitrate and phosphorus and 30 min of COD. Thus, equilibration time was considered thus deemed sufficient for the removal using composite POFA. The pH of the effluent was kept at 6 for COD, nitrate and phosphorus removal but the optimum conditions for ammonia nitrogen removal is pH 9. The ideal conditions were established at dosage of 8 g.

Modification of raw POFA to composite POFA increased the surface area, and larger the surface area of an adsorbent larger the area available for adsorption to take place. Hassani et al. [47] reported that the microstructure of POFA has high BET surface area of 23.75 m² g⁻¹ due to the dispersion of highly porous and irregular shaped particles. However, results show that composite POFA has better BET surface area of 48.6773 m² g⁻¹. The composite POFA apparently contained a high amount of calcium silicate, which was confirmed by SEM and XRD analyses. This indicates the presence of silicon-based material. Other chemical component found in composite POFA is quartz. Conclusively, fundamental batch adsorption studies imply that composite POFA has an excellent potential for removing COD, ammonia nitrogen, nitrate and phosphorus from sewage wastewater. The rapid uptake and high adsorption capacity, coupled with its natural abundance in the environment, are representative of its attractiveness as a low-cost adsorbent, which can be used in versatility in the wastewater treatment applications.

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References


