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# Adsorption efficiency and isotherm of COD and $NH_3$–N removal from stabilized leachate using natural low-cost adsorbent green mussel (*Perna viridis*)

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**ABSTRACT**

Landfills are an important physical facility to disposing municipal solid waste in developing countries. Although, such landfills are correlated with leachate production, which if left untreated, can pose a serious threat to human health and affect the ecosystem in the aquatic life. In the present research study, green mussel adsorbent was explored for the treatment of stabilized landfill leachate. To remove the organic constituent (COD) and ammoniacal nitrogen ($NH_3$–N). The optimum agitation speed, pH, and adsorbent dosage were tested using particle size ranges from 2.00 mm to 3.35 mm. The physicochemical characterization was then determined. The best optimum shaking condition was determined at 200 rpm, pH and adsorbent dosages were 7 and 2.0 g. The optimum percentage removal values for COD are 40% at 200 rpm, 60% at pH 7, and 65% at 2.0 g and the optimum percentage removal values for $NH_3$–N are 30% at 200 rpm, 50% at pH 7, and 45% at 2.0 g, respectively. Generally, the finding results revealed that the Langmuir model adsorption was slightly better fitted and suitable for organic constituent (COD) and Freundlich was good for ammoniacal nitrogen reduction in terms of coefficient of determination ($R^2$). Langmuir adsorption coefficient of determination ($R^2$) for COD are 0.9979 and Freundlich adsorption coefficient of determination ($R^2$) for ammoniacal nitrogen are 0.9938 respectively. This implies that adsorbate adsorption occurs by monolayer adsorption on a homogeneous surface. Therefore, it is proposed that kinetic adsorption be taken into account for further research to examine the organic constituents (COD) and ammoniacal nitrogen process on to the green mussel (*Perna viridis*) media respectively.

*Keyword:* Adsorption; Ammoniacal nitrogen; Green mussel; Leachate; Organic constituent

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## 1. Introduction

Nowadays, population growth in most countries is leading to a rise in industrial and economic growth. This has been affected by the increase in the generation of municipal solid waste (MSW). MSW produced variety of waste from various sources, that is, industrial, municipal, residential, and agricultural), one of which in itself is heterogeneous [1]. The amount of MSW compositions differs for each region and up to 95% of MSW generated and reportedly disposed of in landfills [2]. Landfilling has becomes a significant option for disposing and managing solid waste as this alternative offer throws up a higher amount of MSW at an economic cost than other methods [3]. However, the main drawback of this method is production of extremely polluted leachate which contaminates groundwater and causes a serious environmental problem [4]. Leachate is a high-strength waste water known as one of the most severe common sources of contamination. This liquid, leachate is hazardous and severely contaminated water, produced by solid waste in groundwater as a result of rainwater and moisture. Landfill leachate has a high organic content, high ammoniacal nitrogen content, inorganic salt, chlorinated organics and heavy metal [5]. The untreated landfills leachate is a potential causes of environmental pollution, especially hydro-geological and soil surface pollution. The treatment of landfill leachate is very complex, costly and usually involves several processes [2]. In recent years, there have been many research studies conducted around the world in landfill leachate treatment using numerous type of individuals and/or combination of treatment technology approaches such as physicochemical and/or combination of biological and physico-chemical treatment [4].

In present years, the physicochemical technique has become of great interest in landfill leachate treatment. Landfill leachate treatment uses a variety of technology such as air stripping, oxidation ponds (OP), reverse osmosis (RO), chemical precipitation, ion exchange, membrane filtration techniques, and adsorption [2]. Recent applications have been of great interest in the wastewater treatment of natural indigenous material and low cost material, for example, palm oil ash [6], natural zeolites [7], limestones [8], and especially as adsorbents [9].

Numerous traditional landfill leachate procedures involved, high technology methods are used. In order to meet the discharge standard, the residues produced by traditional methods are saddled with initially high operational cost and lower utilization of several different pollutants, among others [10–17]. An increasing number of studies have been carried out in recent years by other authors (for example agriculture waste or by-products of natural polymer and industrial processes) seeking effective lactate treatment or seeking treatment for alternative conventional media methods. Looks like it does. Polluted water, which includes polluted water.

For example, since potential treatments for kitchen waste water, gravel sand and peat dust have been explored, fruit waste has also been studied to extract heavy metal from wastewater, and some crops have been postulated to remove heavy metal from specific contaminated soils [18–20]. Although activated carbon adsorption is extremely prevalent, the use of green mussel shells (GM) in the treatment of landfill leachate as an alternative to traditional media is concentrated in only a few studies. The treatment of landfill leachate is complex, expensive and most notably involves different processes. Some technologies are useful for the landfill leachate treatment for example, chemical precipitation, chemical oxidation, reverse osmosis, air stripping, membrane filtration, and adsorption. These treatment technologies for treatment of leachate with a focuses on their technological performances. Future works focuses on the study of various promising treatment techniques, especially the physico-chemical techniques is most promising and useful treatment techniques for the stabilized leachate via adsorption [21].

Adsorption or physicochemical technique is relatively simple and might be utilized effectively for the stabilized landfill leachate treatment. Adsorption is basically a process of mass transferring from a substance state of liquid phase to the solid surfaces, becoming bounded physical–chemical interaction. Nowadays, increasing more focus on use of low cost material namely natural or agriculture waste, industrial process by-products, to achieve proper landfill leachate treatment, or due to local availability and environmental friendly material, conventional adsorbent is an alternative approach for the water and wastewater treatment [23].

Adsorption is a valuable technology in the treatment of wastewater. It is very popular method among other methods. The main advantage of adsorption technique is technologically simple, effective, low cost, high capacity and adaptable to many treatment formats. The disadvantage of this method is regeneration is expensive, loss of materials, ineffective against disperse and economically non-viable for certain industries (pulp and paper, textile, etc.).

The author, using the mixture of granular activated carbon and cockle shell for removal of COD and ammonia nitrogen from the stabilized landfill leachate at Simpang Renggam municipal landfill in Johor, Malaysia. It has a high concentration of COD (1,763 mg/L), ammonia nitrogen (573 mg/L) and $BOD_5$/COD ratio 0.09. The adsorption isotherm result reveals that the Langmuir isotherm is best suited to experimental data as compared to Freundlich isotherm [24]. The author, using chemically activated sugar cone (SCAC) for removal of ammoniacal nitrogen and COD from stabilized leachate at Saponic Labs (anaerobic type), Kampar, Perak, Malaysia found that the use of SCAC as adsorption attempts to get rid of 46.65% ammoniacal nitrogen and 83.61% COD with adsorption capacity were 14.62 and 126.58 mg/L respectively [25].

Generally, there are few studies conducted and information is available on the effectiveness of green mussel as partial replacement of commercial adsorbent such as activated carbon and zeolite in the treatment of leachate. Green mussel as alternative low-cost adsorbents derived from natural materials, agricultural wastes and industrial wastes are locally available materials which may have potential as inexpensive sorbents. In Malaysia, mussel shell is abundantly available as a by-product from seafood industry and regarded as waste and mostly left at dumpsite to naturally deteriorate. Based on the experimental findings by using adsorption method techniques as low-cost effective and proficient for COD/Ammoniacal nitrogen (organic/

inorganic) uptake in stabilized leachate. In this present research study, Single (loose) experiment were conducted to investigate the optimal shaking speed, dose, and pH, for the reduction of organic constituent (COD) and ammoniacal nitrogen ($NH_3$–N) from stabilized landfill leachate.

## 2. Materials and method

### 2.1. Leachate characteristic

The raw landfill leachate samples were manually obtained from Simpang Renggam Municipal Landfill site (SRLS) in 30 L high density polyethylene plastic container. The landfill site is located at 10 53'41.64" North Latitude and 1030 22'34.68" East Longitude. "The SRL site area cover around 6 hectare and aerated lagoon method is used as a process for leachate treatment. SRL site now has been operated more than 12 y old and the total solid waste received by the SRL site receives around 250 tons of solid waste per day which covers three regions (i.e., Simpang Ringgam Region, Batu Pahat Region and Kluang District)". The leachate sample were immediately transported towards lab and preserved in cold room (4°C) initially for the experiment used and to minimize the further chemical and biological reaction in compliance with standard procedure for Examination of Water and Wastewater (APHA, 2012). All chemical analysis were carried out within 48 h [5,26].

### 2.2. Preparation of green mussel shell

In this present research study, green mussel shells were used as an experimental samples. The green mussel shells were collected from various commercial restaurants in Parit Raja, Johor Bahru, Malaysia. The green mussel shells were washed with distilled water for several times to clean and removing impurities and debris that came on it. Afterwards, the mussel shells were crushed into smaller particles by using Milling Crusher machine so that it could be handled more easily. The crushed green mussel shells was then dried in the oven at 105°C for 24 h. Then, the mussel shell were subsequently sorted into particle crushes size from 2.00 to 3.35 mm respectively [27]. The X-ray Fluorescent spectrometer (XRF) S4 pioneer Model (Bruker) was used to determine the chemical properties of media. The XRF analysis was revealed that the main compounds are $CaCO_3$ and Cao for adsorption. The media density was conventionally determined (dry weight (kg) divided by volume ($m^3$). Table 1 illustrates the chemical composition of green mussel.

### 2.3. SEM morphology of green mussel shell

The morphology of green mussel shell was analyzed using scanning electron microscopes (SEM) (model JEOL, JSM-7600F) (5 kV acceleration voltage) at UTHM laboratory. The specimen were applied plasma gold coated using sputter coated machine to prevent any electrical charging. The morphology of green mussel shells before and after adsorption in Fig. 1 were taken at 3000 magnifications. As can be seen in Fig. 1a, the SEM image of green mussel shells before treatment is coarse, irregular and angular particles. After the adsorption process, Fig. 1b shows the SEM image of green mussel shells consists of smooth layered surface, which indicates the pollutants present in leachate water were attached on the surface [30,31].

### 2.4. Fourier-transform infrared spectroscopy (FT-IR) waste mussel shells

Fig. 2 shows the Fourier Transform-Infra Red spectroscopic (FT-IR) (Perkin Elmer Spectrum 100) spectrum analysis of the green mussel led to identifying the before

Table 1
Chemical composition of green mussel

| Type of oxide | This study (%) | Research by [28] (%) | Research by [29] (%) |
|---|---|---|---|
| $CaCO_3$ | 95.6 | – | – |
| Cao | 82.48 | 95.7 | 53.38 |
| $Al_2O_3$ | 0.815 | 0.4 | 0.14 |
| MgO | 0.265 | 0.6 | 0.03 |
| $SO_3$ | 0.688 | 0.7 | 0.34 |
| $Fe_2O_3$ | 0.315 | 0.7 | 0.05 |
| SiO | 0.44 | 0.9 | 0.73 |
| $K_2O$ | 0.375 | 0.5 | 0.02 |

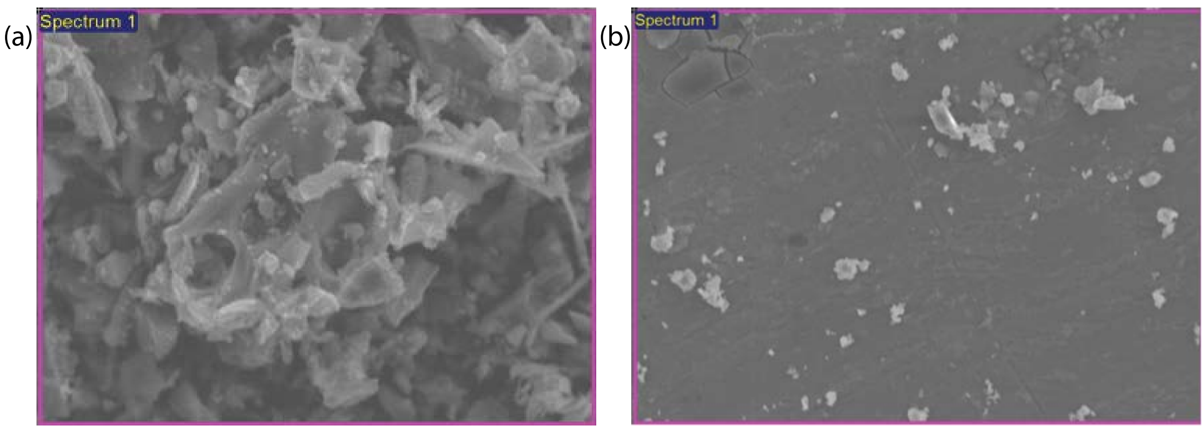


Fig. 1. SEM image of green mussel shells (a) before adsorption and (b) after adsorption in batch experiments.

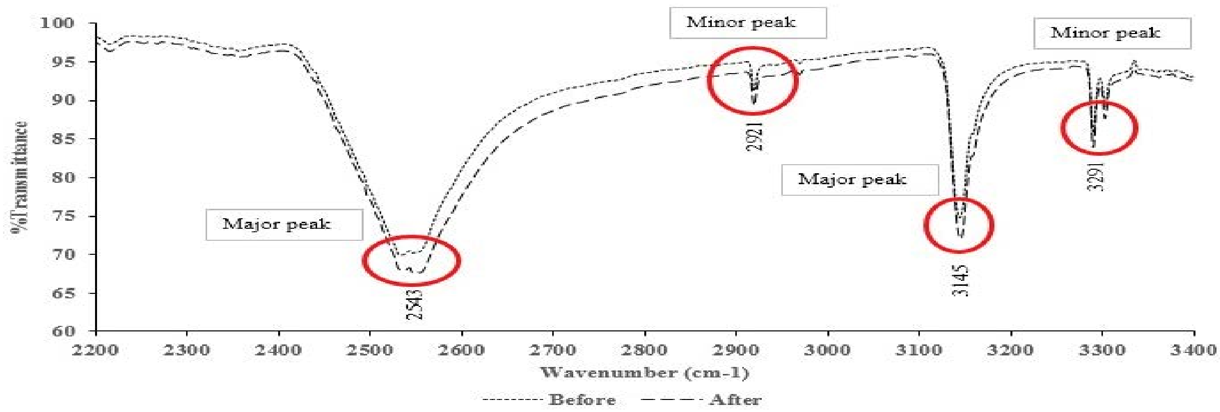


Fig. 2. Green mussel (FT-IR) spectra for before and after treatment.

and after adsorption functional group ranged from 400–4,000 cm$^{-1}$ wavenumbers. The results outcomes of the analysis are described in Fig. 2. Hydroxyls, carbonyls, carboxylic, and amides were a major functional group which is responsible for the process of adsorption. In the case of green mussel, the graph was plotted of wavenumber vs. intensity. Fig. 2 shows four peaks with frequency ranges were recorded from 2,543 and 3,145 cm$^{-1}$. The functional group viz. OH stretches the secondary amine, appeared free at 3,145–3,149 cm$^{-1}$, the surface of the OH group was indicated that one the functional group which are mainly responsible for the adsorption, C–H stretching groups C-methyl appeared at 2,921–2,929 cm$^{-1}$. The chelate compounds peak stretch appeared at 2,543–2,567 cm$^{-1}$ indicates the involvement in N–H stretch frequency in primary amide and C–N stretch frequency appears in aliphatic amine groups at 3,291–3,292 cm$^{-1}$ [32].

## 3. Batch adsorption study

### *3.1. Optimum shaking speed*

Optimization batch study experiment were performed on 250 mL cylindrical beaker contains 100 mL fresh leachate sample and, 4 g of green mussel media was introduced into each flask. The flask was stirred for a specified fix time at ambient temperature using 120 min, pH 7, in an orbital shaker. The optimal shaken speeds (rpm) were determined by adjusting the shaken speed from 50 to 300 rpm. The solution was filtering through a 0.45 µm filtered paper. Organic constituent (COD) and ammoniacal nitrogen both are the main pollutants in landfill leachate have been analyzed. For determination of ammoniacal nitrogen by Nessler's Method, using an UV VIS Spectrophotometer (Model DR6000) and organic constituent (COD) were determined via closed reflux, Titrimetric Method [15,21]. The optimum shaken speeds of samples show optimum percentage removal of COD and ammoniacal nitrogen was chosen as optimum.

### *3.2. Optimum mixing ratio*

The optimum ratio was determined for green mussel for percentage removal of organic constituent (COD) and ammoniacal nitrogen. The optimal shaken speed was used obtained in the previous experiment. The overall mixture of media (4.0 g) was shaking into each flasks. The series of media ratio used for green mussel (GM) were in the order of 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, and 4.0, respectively. The optimal media ratio was achieved by plot the media ratio against the percentage removal. The optimum ratio of media shows optimum percentage removal of COD and ammoniacal nitrogen was chosen as optimum.

### *3.3. Optimum solution pH*

The optimal pH for percentage removal of organic constituent (COD) and ammoniacal nitrogen was calculated by altering by changing the pH of the leachate from 2 to 10. The pH alteration was used 97% H2SO$_4$ (sulfuric acid) and 1M NaOH (sodium hydroxide). The experiments were performed at fixed optimal shaken speeds and optimal mixed ratios after every change to a pH. The optimum pH shows optimum percentage removal of COD and ammoniacal nitrogen was chosen as optimum. The amount of green mussel adsorbed were calculated as percentage removal of organic constituent (COD) and ammoniacal nitrogen according to Eqs. (1) and (2).

$$q_e = \frac{\left(C_0 - C_e\right)V}{m} \quad (1)$$

$$\text{Removal}\left(\%\right) = \frac{\left(C_0 - C_e\right)}{100} \quad (2)$$

## 4. Results and discussion

### *4.1. Chemical analysis of leachate*

Many such reputable research studies published and identify the variation of leachate content from various landfills. The physicochemical characterization of raw leachate are presented in Table 2. The measurements of samples were conducted in triplicates according to the standard methods for the Examination of Water and Wastewater (APHA, 2012). Then the obtained data were compared with data published by previous researchers and MEQA (1974). In this study, a series of experiments were conducted to investigate the adsorption behavior of COD and ammoniacal nitrogen in landfill leachate. Table 2 shows that leachate contains sufficient amounts of organic constituent and ammoniacal nitrogen concentration. The average COD and $BOD_5$ values are 1,829 and 163 mg/L, respectively, and the raw leachate BOD5/COD ratio ranges from 0.07–0.08, within an average of 0.07 (as presented in Table 2). The chemical analysis was performed for following 2 d according with the procedure described in standard Methods for the Examination of Water and Wastewater (APHA, 2012). The adsorption experiment was conducted with same concentration as mentioned in Table 3 without any dilution. The finding result indicates that from the COD and $BOD_5$ values suggesting that the leachate site is evidently stabilized landfill leachate [33–35].

Stabilized landfill leachate is typically high in COD (less than 3000 mg/L) and $NH_3$–N (greater than 400 mg/L) but has a lower ratio of biodegradability ($BOD_5$/COD) [36]. The pH of leachate ranges from 7.65 to 8.27 with an average of 7.96, and it usually increases with time, reflecting the decrease in concentration of the partially ionized free volatile fatty acids (VFAs) [34]. The decrease of VFAs results in an increase in pH. A characteristic pH value for stabilized leachates is around 8 [37]. Previous studies has revealed that for stabilized landfill leachate the concentration of pH is >7.5 [38]. Table 4 shows the physio-chemical characterization result of green mussel. The specific gravity (2.45 g/cm$^3$), surface area (95.95 m$^2$/g), porosity (57.40%), water adsorption (52.62%), methylene blue number (7.97 mg/g), iodine number (21.93 mg/g) and cation exchange capacity (0.80 meq/g) respectively.

### *4.2. Comparative study of COD and ammoniacal nitrogen and adsorption capacity with other adsorbents*

In this study the use of green mussel is consider as novelty as well as to produce the low cost adsorbent for replacement of commercial material (activated carbon and zeolite). Mainly, in this research, the green mussel (*Perna viridis*) adsorbent material are analyzed and compared with the other researcher. While from the analysis, the green

Table 4
Physicochemical characteristics of green mussel media

| Physicochemical properties of composite media | |
|---|---|
| Specific gravity (g/cm$^3$) | 2.45 |
| BET surface area (m$^2$/g) | 95.95 |
| Porosity (%) | 57.40 |
| Water absorption (%) | 52.62 |
| Methylene blue number (mg/g) | 7.97 |
| Iodine number (mg/g) | 21.93 |
| Cation exchange capacity (meq/g) | 0.80 |

Table 2
Physicochemical characterization of raw landfill leachate

| Parameter | Minimum | Maximum | Average | Standard deviation | *Malaysia leachate discharge standard (mg/L) |
|---|---|---|---|---|---|
| COD (mg/L) | 1,595 | 1,829 | 1,712 | 282.51 | 400 |
| Ammoniacal nitrogen (mg/L) | 404.07 | 406.68 | 405.37 | 1.61 | 5 |
| pH | 7.65 | 8.27 | 7.96 | 0.33 | 6.0–9.0 |
| SS (mg/L) | 316 | 367 | 341.5 | 63.22 | 50 |
| Color (Pt-Co) | 4,685 | 4,788 | 4,736.5 | 241.75 | 100 |
| $BOD_5$/COD | 0.07 | 0.08 | 0.07 | 0.02 | – |
| $BOD_5$ (mg/L) | 140 | 163 | 138.66 | 21.81 | 20 |

Acceptable condition for discharging leachate as stated in the 2009 Environmental Quality Regulations, Second Schedule (Regulation 13).

Table 3
Performance comparison with various other researchers

| References | Type of wastewater | Absorbent | Parameter | Removal efficiency (%) |
|---|---|---|---|---|
| [31] | Lake wastewater | Green mussel shell | $NH_4^+$ | 31.28 |
| | | | COD | 44.45 |
| [27] | Leachate | Cockel shell | COD | 55 |
| [21] | Leachate | Activated carbon and green mussel | COD | 83 |
| | | | $NH_3$–N | 63 |
| [22] | River water | Cockel shell | COD | 38.8 |
| Present study | Leachate | Green mussel shell | COD | 65 |
| | | | $NH_3$–N | 45 |

mussel (*Perna viridis*) have shown better performance as compared to other adsorbent materials. Additionally, the overall removal percentage comparison of green mussel (*Perna viridis*) adsorbent is also included in this listed Table 3. From the table, it can be concluded that green mussel (*Perna viridis*) show better removal percentages in terms of COD and ammoniacal nitrogen as compared to other adsorbent material.

The values of isotherm models parameters for the reduction of COD and ammoniacal nitrogen are presented in Table 5. The model parameters are directly related to the variations in the system properties. The result shows the best fitting models and the relative parameters determined for the reduction of COD and ammoniacal nitrogen by adsorbent. Therefore, the Langmuir model was more appropriate to be used to describe the process than the Freundlich model respectively [39].

### 4.3. Determination of optimum shaking speed effect

Fig. 3 demonstrates that the percentage removal of organic constituent (COD) and ammoniacal nitrogen ($NH_3$–N). The experiment were conducted in an orbital shaker ranges between 50, 100, 150, 200, 250, and 300 rpm at room temperature 4°C. The adsorption increases concurrently with shaken speed at the early stage of the adsorption. After reaching 200 rpm, the adsorption also dissipates the shaken speed to a further increasing. Therefore, the removal percentage of COD and ammoniacal nitrogen at 200 rpm (40% and 30%), the adsorption may have reached equilibrium, so that no further improvement can be achieved.

The behavior of the adsorption may attributed initial kinetics energy of the adsorbent and the rate of leachate molecule increases as the shaken speed increased. Consequently, the potential interactions between molecules and adsorbents becomes important. Therefore, the quantity of adsorbent increases, once it enters the equilibrium condition. After once the equilibrium condition reached, the adsorption decreases with varying shaken speed. Therefore, after equilibrium condition may be induced by molecules and adsorbent particles extremely high kinetic energy, which limits their contact with each other [40]. Therefore, 200 rpm was chosen for further research study.

### 4.4. Determination of optimum pH effect

As shown in Fig. 4, the percentage removal of organic constituent (COD) and ammoniacal nitrogen in samples after adjusting the pH value between (2 to 10) and at a shaken speed 200 rpm. It can be shown that the removal percentage of the both parameters by adsorbent gradually increasing at uptake pH 7 (60% and 50%) and decreasing percentage from pH 8 to pH 10 (Fig. 4).

The solution of pH increase, the negatively charge number of site increase, while the positive number of charge site decrease, leading to electro-static attraction between

Table 5
COD and ammonia isotherm constant for activated coconut shell carbon, green mussel, zeolite and composite

| Isotherm (Langmuir) COD | Activated coconut shell carbon | Green mussel (*Perna viridis*) | Zeolite | Composite |
|---|---|---|---|---|
| $R^2$ | 0.9968 | 0.9979 | 0.9944 | 0.9991 |
| $Q$ | 555.56 (mg/g) | 243.90 (mg/g) | 250 (mg/g) | 2,000 (mg/g) |
| $b$ | 0.027 (L/g) | 0.571 (L/g) | 1.06 (L/g) | 0.651 (L/g) |
| $q_e$ | $54.04C_e/1 + 0.0270C_e$ | $142.75C_e/1 + 0.571C_e$ | $588.90C_e/1 + 1.06C_e$ | $158.78C_e/1 + 651C_e$ |
| | | Isotherm (Langmuir) $NH_3$–N | | |
| $R^2$ | 0.9963 | 0.9899 | 0.9974 | 0.9982 |
| $Q$ | 90.90 (mg/g) | 166.67 (mg/g) | 200 (mg/g) | 208 (mg/g) |
| $b$ | 10 (L/g) | 16 (L/g) | 0.175 (L/g) | 3.793 (L/g) |
| $q_e$ | $2,000C_e/1 + 10C_e$ | $3,333.34C_e/1 + 16C_e$ | $29.32C_e/1 + 0.175C_e$ | $344.878C_e/1 + 3.793C_e$ |
| | | Isotherm (Freundlich) COD | | |
| $R^2$ | 0.9965 | 0.9938 | 0.8202 | 0.9974 |
| $K_f$ | 15,980.85459 | 4,027,170.343 | 6,520,786.785 | 3,379,091.874 |
| $1/n$ | 0.7937 | 0.3411 | 0.1709 | 0.3362 |
| $q_e$ | $15,980.85C_e^{0.7937}$ | $4,027,170.342C_e^{0.3411}$ | $6,520,786.785C_e^{0.1709}$ | $3,379,091.874C_e^{0.3362}$ |
| | | Isotherm (Freundlich) $NH_3$–N | | |
| $R^2$ | 0.9514 | 0.9632 | 0.9568 | 0.9667 |
| $K_f$ | 276,312.1614 | 269,649.7364 | 2.30E+51 | 85,921.134 |
| $1/n$ | 0.1281 | 0.1431 | 8.0567 | 0.2995 |
| $q_e$ | $276,312.1614C_e^{0.1281}$ | $269,649.7364C_e^{0.1431}$ | $2.30E+51C_e^{8.0567}$ | $85,921.134C_e^{0.2995}$ |

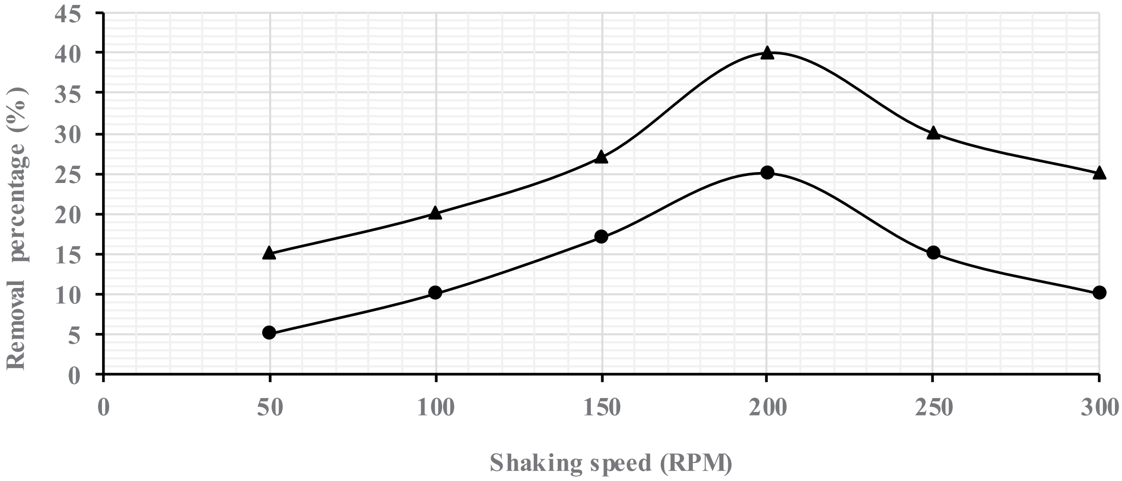


Fig. 3. Optimum shaking speed for removal of COD and $NH_3$–N at 50,100,150,200,250 and 300.

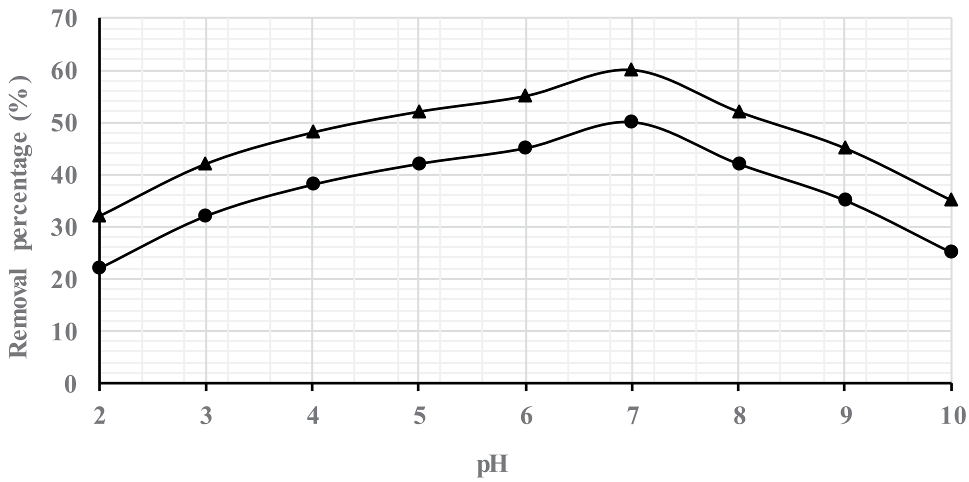


Fig. 4. Optimum pH for removal of COD and $NH_3$–N at 2, 3, 4, 5, 6, 7, 8, 9, and 10.

charge particle. The uptake adsorption processes increase until it achieve equilibrium condition. With an increase in pH 8, the decrease in uptake may be due to the dissociation that takes place in the solid to liquid range due to acid and base interactions [41]. The optimum condition of pH 7 for removal of COD and ammoniacal nitrogen was chosen for further research study (Fig. 4).

### *4.5. Determination of optimum adsorbent dosage effect*

The determination of adsorbent dosage effect on adsorption was calculated within shaken speed value 200 rpm, pH value 7, and dosage varying from 0.0 to 4.0 g. In first instant, removal efficiency increasing until reaches optimal adsorbent mass 2.0 g (65% and 45%). After that, the removal percentage begins to decrease with further increase in the dosage (Fig. 5). This behaviors described by the fact that the adsorbent dosage amount increasing, the adsorption amount of available site increases, until reaches optimal adsorbent mass. Moreover, any additional increase in adsorbent dosage results in aggregated, which reduces the chance of molecular interaction with all available adsorption site [42,43].

### *4.6. Adsorption mechanism*

The mechanism of optimization process such as mixing media, shaking speed, and pH findings result indicates that the mixing media for green mussel in the treatment of COD and ammoniacal nitrogen is 2.0 g and that the optimum shaking speed of the media is 200 rpm, pH 7, and adsorbent dosage 2.0 g, respectively.

Moreover, adsorption isotherm model were applied to the experimental data in order to analyze the rate of adsorption and possible adsorption mechanism of COD and ammoniacal nitrogen onto green mussel. From Figs. 6 and 7 it can be observed that the Langmuir Isotherm model provide a better fit to the experimental data whereby the value of coefficient of determination ($R^2$) of COD and ammoniacal nitrogen for green mussel was 0.9979 and 0.9899 respectively. On the other hand, the Freundlich Isotherm model obtained the coefficient of determination ($R^2$) of

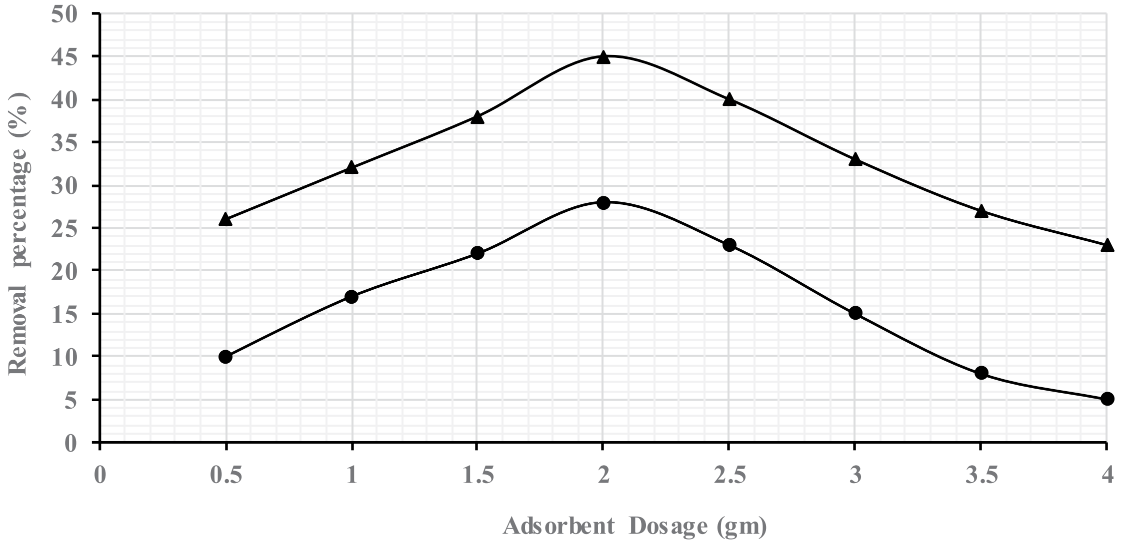


Fig. 5. Optimum adsorbent dosage for COD and ammoniacal nitrogen removal.

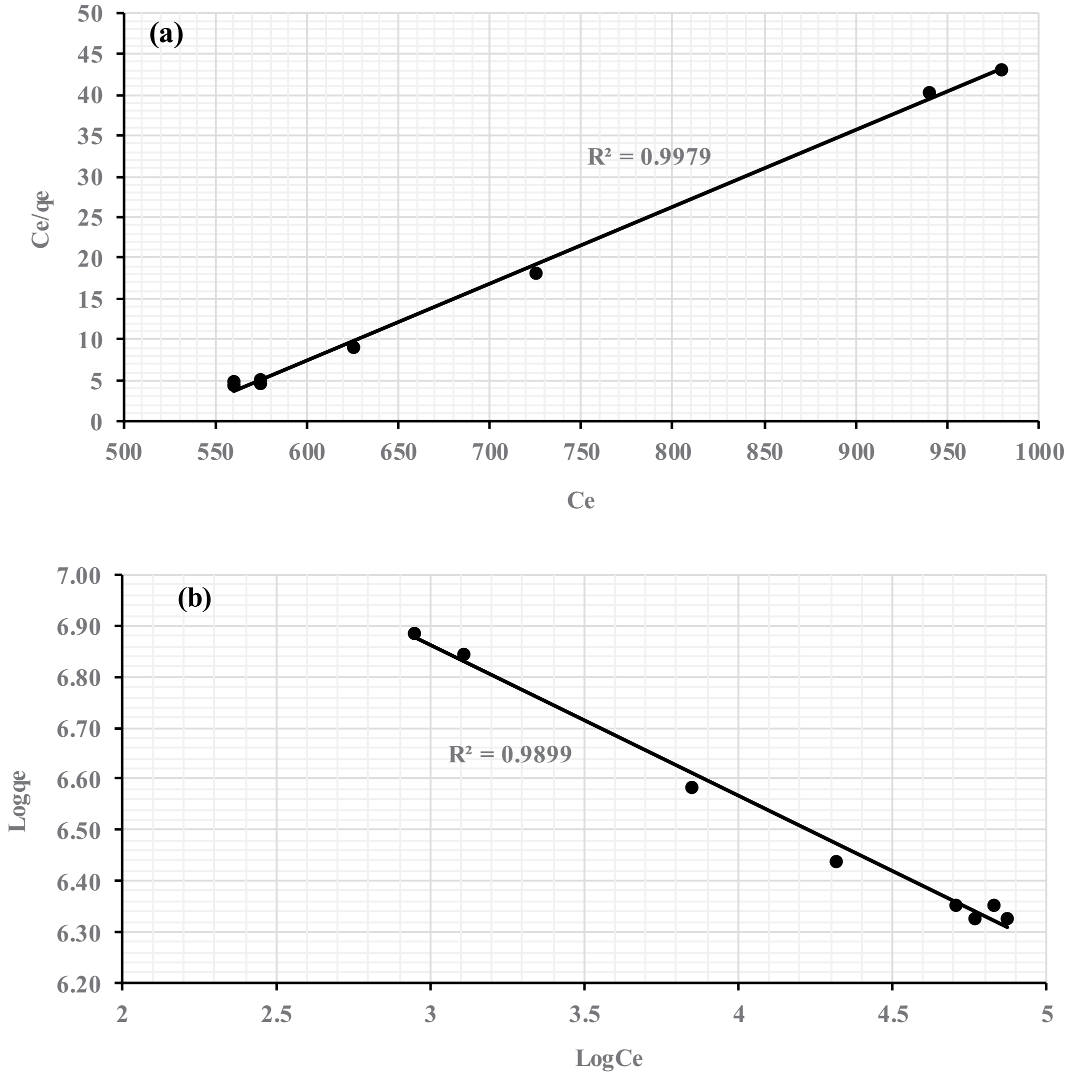


Fig. 6. Isotherm models for COD removal (a) Langmuir and (b) Freundlich.

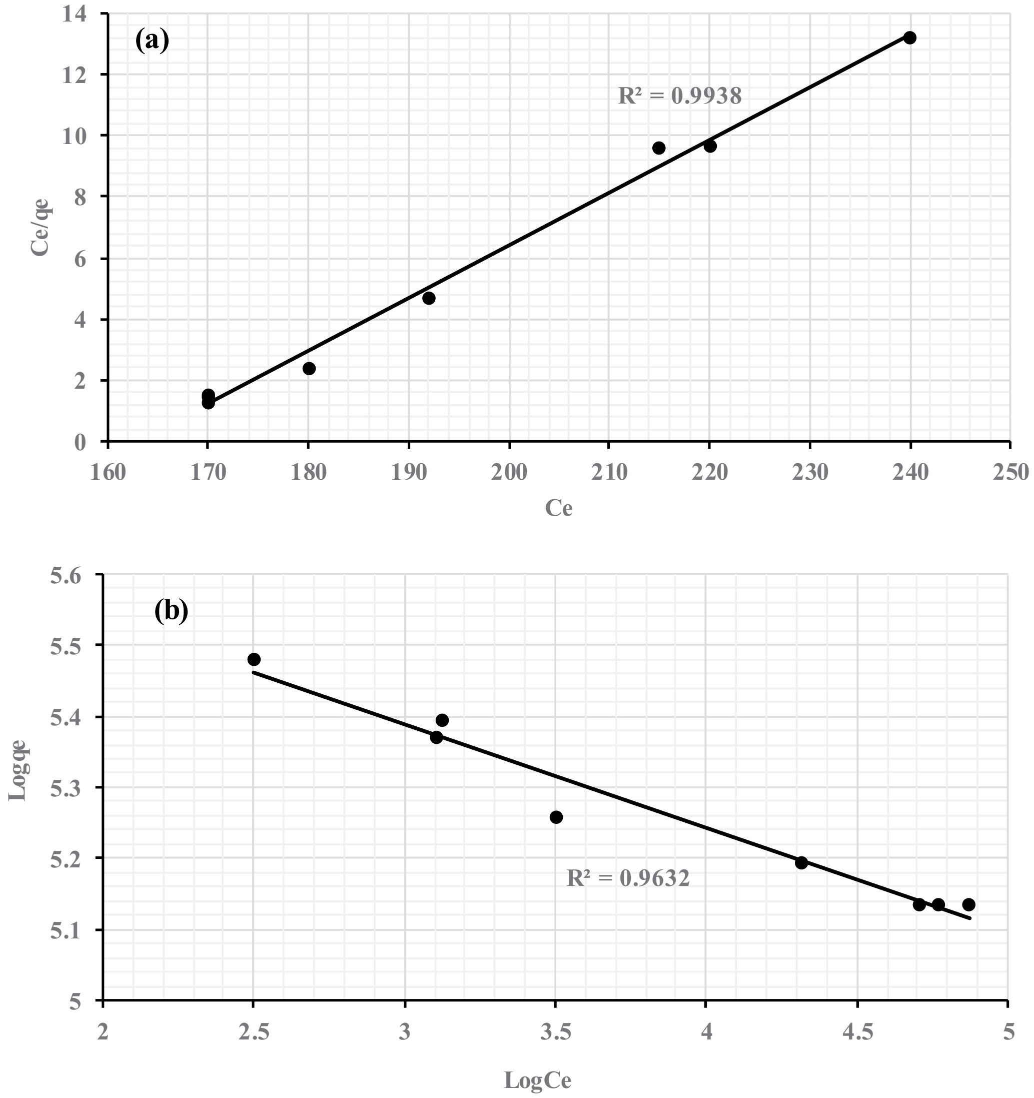


Fig. 7. Isotherm models for $NH_3$–N removal (a) Langmuir and (b) Freundlich.

0.9938 for (COD) and 0.9632 for (ammoniacal nitrogen). Thus, this result showed that the adsorption of COD and ammoniacal nitrogen obey the Langmuir Isotherm model.

### *4.7. Adsorption equilibrium*

The equilibrium adsorption condition is usually formed on the isothermal adsorption (*X*- and *Y*-axes) plotting in the form of adsorbed amount and mass adsorption in the flow fluid (at constant temperatures). The isothermal research study describes the adsorption mechanism and contact between adsorbent–adsorbate surfaces. For equilibrium adsorption system isotherm (Langmuir and Freundlich) equations has been extensively used.

#### *4.7.1. Langmuir isotherm*

Freundlich and Langmuir isotherm models are usually applied to describe the adsorption processes between the sorbate and sorbent molecules in an aqueous solution. In this work, isotherm models such as Freundlich and Langmuir were applied to evaluate the sorption process. According to the Langmuir model; all the accessible sorption sites are homogeneous and morphologically uniform [44]. Langmuir model equation is given by;

$$\frac{1}{q_e} = \frac{q_m K_l C_e}{1 + K_l C_e} \tag{3}$$

where $q_e$ = equilibrium sorption capacity (mg g$^{-1}$), $C_e$ = equilibrium concentration of the adsorbate (mg L$^{-1}$), $q_m$ = maximum amount of adsorbent per unit weight of adsorbent (mg g$^{-1}$), and $K_l$ = Langmuir constant related to binding sites affinity with adsorbent (L mg$^{-1}$).

#### *4.7.2. Freundlich isotherm*

The Freundlich model defines adsorption as a reversible multilayer process over heterogeneous [45]. The model equation is represented by;

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

where $K_f$ = Freundlich constant, $n$ = constant relating to adsorption intensity and $C_e$ = equilibrium concentration of the adsorbate (mg L$^{-1}$).

The values of isotherm models parameters for the removal of COD and ammoniacal nitrogen are presented in Figs. 6 and 7. The parameters of the model are related to variation in the properties system. The finding results indicates better fitted models and relative parameter determined for the removal of COD and ammoniacal nitrogen by the adsorbent. The table also show that Langmuir model was in accordance with experimental data for the removal of contaminants investigated with coefficient of determination ($R^2$) value of 0.9798 and 0.9920 for COD and ammoniacal nitrogen respectively. Therefore, the Langmuir model was more appreciate to be used to describe the process than the Freundlich model.

## 5. Conclusion

This study investigates the ability of green mussel (*Perna viridis*) to minimize organic constituent (COD) and ammoniacal nitrogen from stabilized leachate. The static batch experiment finding result was indicates that optimal ratio of green mussel media in treatment of organic constituent (COD) and ammoniacal nitrogen was 2.0 g and the optimal shaking speed were 200 rpm. The optimal pH was 7. The research findings expand the existing literature on alternative media for leachate treatment, especially in developing countries. Generally, the finding results revealed that the Langmuir model adsorption was slightly better fitted and suitable for organic constituent (COD) and Freundlich was good for ammoniacal nitrogen reduction in terms of coefficient of determination ($R^2$). Langmuir adsorption coefficient of determination ($R^2$) for COD are 0.9979 and Freundlich adsorption coefficient of determination ($R^2$) for ammoniacal nitrogen are 0.9938 respectively. This implies that adsorbate adsorption occurs by monolayer adsorption on a homogeneous surface. Therefore, it is proposed that kinetic adsorption be taken into account for further research to examine the organic constituents (COD) and ammoniacal nitrogen process on to the green mussel (*Perna viridis*) media respectively.

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