Kinetic and isotherm studies of empty fruit bunch biochar on ammonium adsorption

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Abstract. The presence of excessive ammonium in wastewater due to agriculture and other industrial activities affects the aquatic plants, animals and human health. Common wastewater practice offers high cost and maintenance as well as low performance. The adsorption technique offers an efficient, economically favourable and reliable physicochemical treatment method. Despite the efficiency, the studies on Empty Fruit Bunch (EFB) biochar as an adsorbent for ammonium removal is under discovered. The conducted study described the characterization of EFB biochar together with its kinetic and isotherm studies for ammonium removal. EFB underwent conventional pretreatment using fixed bed reactor at temperature of 350, 450, 550 and 650 °C for 60 min of holding time prior for characterization and kinetic studies. For characterization studies, moisture, ash and pH analysis were performed before proceed with adsorption and kinetic studies. It was found that the increment of temperature resulted in high content of ash and low content of moisture while optimum pH was in the range of pH 7. The optimum condition for ammonium adsorption was 2.5 ppm of EFB, 0.05g of ammonia dosage and time exposure of 200 minutes. The ammonium adsorption followed the pseudo-second-order kinetic model which suggests that the ammonium adsorption process is controlled by the chemical adsorption mechanism. The finding suggests the utilization of EFB biochar as a good alternative for ammonium removal through adsorption process while increasing the biomass value.

1. Introduction

Ammonium presents in water may have harmful effects to aquatic plants, animals and human health. It’s being discharged together with agricultural, municipal and industrial waste that are contributed to harmful effects such as decreased dissolved oxygen, increase corrosion rate of soil materials, toxicity to aquatic life and eutrophication of lakes and rivers [1]. Current technologies being used for the removal of ammonium such as air stripping, reverse osmosis and ion exchange suffer high cost and high maintenance. Besides, the traditional method, which is biological treatment reveals a low performance in the removal of high concentration of ammonium [2]. In comparison with those method, adsorption possess an efficient, economically favourable and reliable physicochemical treatment method. Moreover, adsorption can be considered as a better choice in water treatment because it is convenience, ease of operation and simple design.
Biochar is a porous and carbon rich solid which frequently produced by slow pyrolysis of agriculture waste with or without the presence of oxygen [3–5]. The most abundant wastes in palm oil production industry is empty fruit bunch that generates about 50 million tonnes per year worldwide [6]. Dumping of empty fruit bunch (EFB) from the palm oil production trade has caused the production of leachate which can seep into the ground and lead to an environmental hazard. Other than that, the incineration of EFB can cause air pollution. Since EFB is high carbon content and rich in lignin, it can be a good choice for the production of adsorbent in adsorption process which is widely used in water treatment industries [7]. Hence, this would provide an optimal supply chain for biochar production using EFB as a feedstock.

Therefore, this study aims to evaluate the potential of empty fruit bunch (EFB) biochar as an adsorbent for removal of ammonium through adsorption process. At the same time, kinetic and isotherm studies were performed to find out the adsorption process mechanism analysis.

2. Methodology

2.1. Materials
EFB samples were obtained from palm oil industries in Kedah, Malaysia. Ammonium, phenol, ethyl alcohol, sodium nitroprusside, sodium hydroxide, sodium citrate, sodium hypochlorite were purchased from Qrec (Germany).

2.2 Preparation of adsorbents
EFB obtained after extraction from the fresh fruit bunch (FFB) usually have a moisture content of 12% resulting from the milling process for oil production [8]. Hence, the EFB collected for this study were washed first with distilled water to get rid of impurities and surface oil and dried in oven [9]. Normal drying process to remove moisture content in EFB take more than 24 hours. In this study, the EFB were dried at 105°C for about 48 hours in a conventional oven in order to avoid any growth of orange fungus and grey mould [10-12]. The dried EFB was ground using grinder into small size [13, 14]. Then, the dried EFB was sieved and separated into fraction of different sizes, of 250µm by using a sieve shaker [15-19]. Roughly, 100g of dry EFB sample was weighed on the electronic mass. Then, it was placed into the porcelain crucible. Next, the porcelain crucible was placed in the muffle furnace for pyrolysis processes. The pyrolysis of the dry EFB was performed at four different peak temperatures which were 350°C, 450°C, 550°C and 650°C at a heating rate of 30°C/min and residence time of 1 hour as pyrolysis variables in order to determine the impact on adsorption properties of the biochar produce [20]. EFB biochar that is produced at pyrolysis temperature of 350°C is denoted as EFB350 in the subsequent discussion. The same applies to EFB pyrolysed at EFB450, EFB550 and EFB650 °C.

2.3 Characterization of biochars
The moisture and ash content of EFB biochar were determined according to ASTM E1756-08 and E1755-01 methods respectively. The analyses involved measurements of weight loss following combustion of 2 g sample in a ceramic crucible at 105°C and 600°C respectively, until constant weight was achieved. The pH value of the adsorbent at point of zero charge (pHpzc) was determined using potentiometric titration [21]. A series of 50 mL solutions with initial pH (pH initial) between 3.0 and 11.0 were prepared and 0.25 g of TSB adsorbents were placed in each flask followed by agitation at 200 rpm for 48 h. Next, the final pH value (pHfinal) of the solution with each sample was measured.

2.4 Adsorption studies
The ammonium stock solution with 1.0 g/L concentration was prepared by dissolving 3.82 g/mol of ammonium in 1 L of distilled water in a volumetric flask. 100 ml of Erlenmeyer flasks was used to contain the 50 ml ammonium solution and the biochar. It was shaken at 200 rpm for 120 min at 25°C. Lastly, the supernatant was filtered. The amount of ammonium ions exchanged by the biochar was analysed by UV-Vis spectrophotometer according to phenate method. For the phenate method, about 25 ml of the ammonium solution was added into a flask which contained 1.0 ml of phenol solution, 1.0 ml
of sodium nitroprusside and 2.5 ml of oxidizing solution and then stirred together. The mixture was covered with plastic wrap and waited for 1 hour before concentration determination by UV-Vis spectrophotometer.

3. Results and discussion

3.1 Analysis of physical and chemical biochar

The moisture and ash contents of biochar at different temperature is shown in table 1. The EFB350 biochar has the highest moisture content, followed by EFB450, EFB500 and EFB550. Apparently, the moisture content in the biochar samples decreased as the pyrolysis temperature increased from 350 °C to 550 °C. Obviously, when the pyrolysis temperature is increased, the rate of drying of the EFB biochar samples increased too [22].

| EFB Biochar | Moisture content (%) | Ash Content (%) |
|-------------|----------------------|-----------------|
| EFB350      | 7.1                  | 49.06           |
| EFB450      | 5.93                 | 57.80           |
| EFB500      | 5.91                 | 69.36           |
| EFB550      | 5.90                 | 93.13           |

Biochar produced from EFB is relatively fine and contain high amount of ash compared to other feedstock [8]. From table 1, the ash content of EFB350 biochar sample is 49.06 % which increases gradually to 57.80, 69.36 and 93.13 % when the pyrolysis temperature is increased to 450, 500 and 550 °C respectively. The results are in good agreement with Devi (2015) [23]. The increasing trend can be explained in terms of the presence of the catalytic volatilization of the organic matter in existence of inorganic minerals that exist within the EFB biochar. Usually, ash consists of inorganic elemental oxides in terms of bulk mineral matter; while carbon (C), oxygen (O), sulphur (S) and water underwent devolatilization process during the pyrolysis [24, 13]. From table 1, EFB450 is considered as the best biochar sample to be used for the adsorption process. EFB450 contains an average amount of ash and it showed only a slight difference with EFB350 which is considered as not significant towards the adsorption process.

The main purpose of the pH zero charge is to determine the pH at which the biochar has zero charges and the surface has zero electrical charge density. The biochar samples, EFB350, EFB450, EFB500 and EFB550 were used for determining the pH zero charge of the samples. Figure 1 shows the graph of pH zero charge for EFB350, EFB450, EFB500 and EFB550. The surface chemistry of any material is determined by the acidic (positive surface charge) or basic (negative surface charge) character of their surface. In adsorption studies, it is very important to know the surface charge of the material used because a high surface area material may be produced. From figure 1, the pH zero charge of the biochar samples is in the region of 7.0, meaning that the pH zero charge of the EFB biochar samples has a neutral condition. Therefore, pH 7 is used as constant pH in the ammonium solution for the adsorption process test.
3.2 Analysis of biochar on adsorption process

The effect of adsorbent dosage on the rate of removal of ammonium was examined using different dosage of EFB biochar such as 0.05, 0.10, 0.15, 0.20 and 0.25 g. According to figure 2, the adsorption capacity of ammonium decreased from 2.49 to 0.46 mg/g upon contacted with EFB adsorbent at the different dosage from 0.05 to 0.25 g. The highest adsorption capacity was recorded at 0.05 g due to the high surface area and the availability of the adsorption sites for ammonium removal. Increased in the adsorbent dosage beyond 0.10 g results in a reduction of the adsorption capacity. The result was in good agreement with Radnia et al. [25], where the adsorption capacity decreased with the increase of adsorbent dosage since more active sites remained uncovered during the adsorption process.

The excess of biochar added for adsorption of ammonium, the more adsorption sites are provided so that the ammonium is easily absorbed by the active sites. However, the addition of dosage increased in the concentration which lead to adsorption competitive on the active sites. Due to the adsorption competitive, the adsorption capacity of ammonium removal will reduced gradually. Therefore, the optimum adsorbent dosage for the adsorption capacity of the ammonium was 0.05 g.

The effect of adsorption contact time was analysed at initial concentration of ammonium 2.5 ppm, temperature of 30 °C with speed of 150 rpm, adsorbent (EFB) dosage of 0.05 g and pH 7. The results are as shown in figure 3 at different contact time with the adsorbent is between 5 and 240 minutes. The results show a relatively rapid uptake of ammonium at the initial period and reaches a steady state (equilibrium) towards the end of the adsorption process. The early rapid phase may possibly due to the contribution of a large number of vacant sites present [26]. The number of vacant sites decreased over time that created the concentration gradient between solution and adsorbent where a slower adsorption would follow as the available adsorption site were gradually decreased. Since the value of adsorption capacity at 200 and 240 minutes remained constant, it is suggested that the adsorption already reached equilibrium at 200 minutes. Subsequently, any further increased in adsorption contact time would not enhance the ammonium adsorption. Thus, the optimum adsorption contact time for the ammonium adsorption was at 200 minutes.

Figure 4 illustrates the adsorption capacity of ammonium increases with increasing initial concentration of ammonium from 0.5 - 3.0 ppm. When the initial concentration of ammonium is increased, the mass transfer driving force increases too. The ammonium ion removal process is and extremely concentration dependent process as being endorsed to the mass transfer effects where concentration of driving force is directly proportional to the initial concentrations [25]. At high initial concentrations, the active sites of the biochar were surrounded with more ammonium ions in the solutions and vice versa. Therefore, the adsorption capacity of ammonium increases with the increasing of ammonium concentration which boosts up the adsorption process. The optimum initial concentration of ammonium was 2.5 ppm.
Figure 2. The adsorption capacity of ammonium, $q_e$ (mg/g) against adsorbent dosage (g).

Figure 3. The adsorption capacity of ammonium, $q_e$ (mg/g) against contact time, $t$ (min).

Figure 4. The adsorption capacity of ammonium, $q_e$ (mg/g) against initial concentration of ammonium (ppm).
3.3 Analysis of kinetic study in adsorption process

From figure 5 and 6, both graphs show different patterns. By comparing the value of $R^2$ from both graphs, pseudo-second-order model gives higher value of $R^2$ which is 0.9999 that is close to 1 as compared to pseudo-first-order model with a $R^2$ value of 0.9767. Instead of comparing the value of $R^2$, the non-linear Chi-square ($X^2$) determination was also used in order to find the appropriate kinetic model for the ammonium adsorption process. The value of $X^2$ indicates the difference between the value of $q_{\text{experimental}}$ and $q_{\text{calculated}}$. If data from the model are similar to the experimental data, the value of $X^2$ should have a small number. In case the values from model are different from experimental value, $X^2$ should have be a bigger number.

![Figure 5](image_url1)

**Figure 5.** The pseudo-second-order model, $t/q_t$ against adsorption contact time (min).

![Figure 6](image_url2)

**Figure 6.** The pseudo-first-order model, ln ($q_e - q_t$) against adsorption contact time, $t$ (min).

Table 2 shows the different in value of $R^2$ and $X^2$ for both, pseudo-first-order model and pseudo-second-order model. The pseudo first-order model gives a bigger value of $X^2$, 1.2175 while pseudo-second-order $X^2$ is 0.2210, a smaller number. In order to determine the best kinetic model, higher $R^2$ and low $X^2$ values are preferred and confirmed to be the best-fit expression to represent the kinetic model [27]. As can be seen from table 2, pseudo-second-order model has a better correlation of experimental data as it has a higher value of $R^2$ (0.9999) and low value of $X^2$ (0.2210). Therefore, the ammonium adsorption by EFB biochar followed the pseudo-second-order kinetic model which suggests that the ammonium adsorption process is controlled by the chemical adsorption mechanism. Chemical
adsorption explained that the adsorbate adheres on the adsorbent by formation of a chemical bond and searched for sites that maximized their coordination number with the surface [28].

Table 2. Kinetic parameters for ammonium adsorption.

| Kinetic Model       | Linear regression | Parameter | Value of parameter |
|---------------------|-------------------|-----------|--------------------|
| Pseudo-first-order  | $y = -0.0187x - 0.5296$ | $R^2$     | 0.9767             |
|                     |                    | $X^2$     | 1.2175             |
| Pseudo-second-order | $y = 1.2907x + 4.0931$ | $R^2$     | 0.9999             |
|                     |                    | $X^2$     | 0.2210             |

### 3.4 Adsorption isotherm

In terms of adsorption isotherms, Langmuir and Freundlich isotherms were frequently used in order to investigate the relationship between the solid surface adsorption capacity and the equilibrium adsorption of solute in the solution [26]. Langmuir adsorption isotherm is based on the homogeneous surface of active sites and a monolayer adsorption process. Meanwhile, Freundlich adsorption isotherm is applied based on multilayer adsorption process on a heterogeneous surfaces [29]. The equilibrium data for ammonium adsorption by EFB450 biochar were fitted in order to describe the experimental data of adsorption isotherms. Figure 7 and 8 shows the graph of Langmuir isotherm and Freundlich isotherms respectively.

![Graph of Langmuir isotherm](image1)

**Figure 7.** The Langmuir isotherm, $Ce/q_e$ against equilibrium concentration, $Ce$ (ppm).
Figure 8. The Freundlich isotherm, ln q_e against ln Ce.

Table 3 shows the parameters for both Langmuir and Freundlich isotherms. The values of R^2 for Freundlich isotherm is 0.991 which is higher than the R^2 value from Langmuir isotherm which is 0.8436. The higher value of R^2 describes that the experimental data of adsorption process is best fitted with that isotherm. However, the Chi-square, X^2 value must also be considered in order to determine the best isotherm model for the adsorption process. The Chi-square, X^2 analysis is basically the sum of the squares of the differences between the calculated data and the experimental data obtained. The R^2 and Chi-square, X^2 values seem to be well fitted with Freundlich isotherm since the value of R^2 is 0.991 and smaller X^2 value of 3.1478 compared to Langmuir isotherm which are 0.8436 and 10.8196 respectively. It is clear that Freundlich isotherm is the best-fitting model for the adsorption of ammonium by using EFB450 biochar. This indicates that the ammonium adsorption process was a heterogeneous adsorption of the multi molecular layer [30].

| Isotherm Model      | Linear regression | Parameter | Value of parameter |
|---------------------|-------------------|-----------|--------------------|
| Langmuir Isotherm   | y = -0.3822x + 0.1582 | R^2       | 0.84               |
|                     |                    | X^2       | 10.82              |
|                     |                    | R^2       | 0.99               |
| Freundlich Isotherm | y = 1.4556x + 3.2153 | X^2       | 3.15               |

4. Conclusion
The present study revealed the potential of EFB biochar as a good adsorbent especially for waste water treatment in removal of ammonium through adsorption process. Hence, this would provide an optimal supply chain for biochar production using EFB as a feedstock. The best ammonium adsorption condition was 2.5 ppm of EFB biochar, 0.05 g of ammonia dosage and time exposure of 200 minutes. The kinetic and isotherm studies showed that the adsorption process followed Freundlich isotherm, reflected to the heterogeneous adsorption of the multi molecular layer. Further and deeper studies are inevitably needed to be performed for scale up adsorption process. The application of EFB biochar therefore, enhance the utilization of biomass from palm oil industries, thus reducing the greenhouse effect while increasing the biomass value.
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