The Prospect of Biochar by Oil Palm Empty Fruit Bunch (OPEFB) in the Removal of Contaminants Emerging Concern (CECs)

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> **Abstract.** Although pharmaceuticals are detected at low levels, their continued release into the environment might result in significant long-term concentrations and lead to damaging consequences on humans, animals, and the environment. The findings have been analysed that various pharmaceutical components were found in sewage treatment plants, including naproxen sodium. Naproxen sodium has been found in various water sources, such as in groundwater and in drinking water. Utilizing OPEFB as adsorbent in wastewater treatment is a feasible alternative. This study focussed on the adsorption capacity of OPEFB biochar for naproxen removal water. The highest percentage removal (99.7%) of naproxen achieved at 100 ppm concentration with 2.5 g of OPEFB biochar. Meanwhile, the usage of 5.0g of OPEFB biochar showed the highest percentage of the removal of naproxen sodium at 100 ppm concentration after 24 hours was 99.27%. OPEFB is one of the most suitable and have the potential in removing almost all the pollutants in wastewater by undergoing the adsorption process.

1 Introduction

Contaminants of emerging concern (CECs) are one of the major pollutants that contribute to aqueous environment pollution. The pharmaceuticals and personal care products (PPCPs), flame retardants (FRs), pesticides, endocrine-disrupting compounds (EDCs) and artificial sweeteners are examples of the CECs [1]. According to Amin et al. [2], CECs commonly negatively impact aqueous ecosystems and human health. A study has been made by Amin et al. [3,4] shows that CECs are susceptible to poor removal during the conventional wastewater treatment process which has been often detected in the wastewater treatment plant. Undoubtedly that the discharge of effluent treatment by the wastewater treatment plant will make groundwater, watershed and river contaminate as well as the drinking water that has been reported in numerous water samples all over the globe [4-12].

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Nowadays, the latest scientific research focuses on the strategies to reduce CECs effluent based on the advanced and conventional treatment processes [5]. The usage of biochar that acts as an adsorbent is one of the brilliant alternatives for removing the CECs in wastewater due to its porous structure, surface functional groups and large specific surface area [6,11,12]. According to Amin et al [4], the activation of biochar using physical and chemical methods can increase the specific surface area and pore volume which assuredly increases its adsorption capacity. Agriculture wastes like animal waste, plant residues, and plant waste are the common and well-known waste to produce the biochar [4-6]. According to Rasat et al [5], the characteristic of biochar depends on the pyrolysis process and the raw materials used. According to Amin et al [1,2,3,4,10], among other methods mentioned earlier, adsorption is the most auspicious and low-cost technique prior to its scalable processability, high efficiency, and ease of operation. Therefore, oil palm empty fruit bunch (OPEFB) is one of the outstanding agricultural wastes that can help in CECs removal. The OPEFB waste is seen as a promising material that can be used in CEC removal as well as can reduce agricultural waste. By undergoing a torrefaction process to produce the biochar, it can reduce environmental issues like global warming and climate change [5]. The prospective use of OPEFB biochar in naproxen removal is analysed in this study.

2 Material and Methods

2.1 Materials

To produce the biochar, raw oil palm empty fruit bunch (OPEFB) was used to test the adsorption rate of naproxen by undergoing the torrefaction process. To get the adsorption rate results, the naproxen solution was prepared in the Faculty of Earth Science, Environmental research laboratory. The raw OPEFB were collected from Felda Bilut, Raub, Pahang and the naproxen powder was purchased at Sigma Aldrich Sdn. Bhd.

2.2 Preparation of Torrefied OPEFB Biochar

To produce the biochar, the raw OPEFB must be free from impurities and oils, therefore, tap water has been used to wash the OPEFB. After the samples undergo the washing process, the clean samples were dried under direct sunlight for a day. Then, the samples were placed in the oven for further drying at about 85°C for one hour to bring down the moisture content. After that, the dried samples were ground into smaller particle sizes by using a 750μm sieve. By doing so, it is easy to get the desired particle size.

Next, the OPEFB fibres were going through the torrefaction process where the process was the thermal pre-treatment method and has been analysed. In the torrefaction process, 274°C was set as the holding temperature without the presence of oxygen and under a slow heating rate for 90 minutes.

Fig. 1. Raw oil palm empty fruit bunch (OPEFB).

Fig. 2. Torrefied OPEFB biochar.

2.3 Naproxen solutions preparation

The naproxen sodium tablets used in this experiment have a white colour, odourless, round shaped, and crystalline solid. Naproxen sodium is soluble in water and methanol [1]. About 20 g of powdered naproxen sodium is weigh and transferred into the beaker whereby 30 ml of methanol was added to it until dissolved. The undissolved powdered naproxen sodium turned mushy, and it undergoes the air-dried process in the fume chamber to get rid of the remaining methanol. Then, it dissolved in 1 litre of distilled water and placed on the orbital shaker at 200 RPM for seven days to ensure it completely dissolved. The condition of the master solution was cloudy, where the residues of undissolved naproxen were still available. The solution then was filtered before standard solutions were created. After the master solution reached saturation, a stock solution of 1000,500,100, and 50 ppm was created. Each absorbance of the standard solution was measured, and the calibration curve was made. High-Performance Liquid Chromatography (HPLC) was used to measure the absorbance of the standard solutions.

Fig. 3. Naproxen sodium solution calibration curve.

2.4 Absorption Experiment

Five different naproxen concentrations have been set up which were in range of 0-1000ppm with three different masses of OPEFB biochar which were 0g as blank, 2.5g, and 5.0g. The beakers were set aside for 60 minutes. After that, a 10 ml syringe with a syringe membrane filter has been used to extract aqueous samples from the solutions and 5 ml of concentrations were evaluated using a Waters High-Performance Liquid Chromatography Plus Prep. The HPLC was used to separate the mixtures of related substances and determine the mixture's constituent parts, along with analysing the solutions at 0.5 hours, the first hour, and after 24 hours. The HPLC used in this study was equipped with a photodiode array (PDA) detector, the C-18 column as the stationary phase, and the mobile phase used was methanol and acetonitrile. The suitable flow rate in the detection of naproxen sodium was 1 mL/min with a wavelength of 235 nm. The temperature was constant at 30°C.

2.5 Absorption capacity and removal efficiency

This experiment was carried out for 24 hours to achieve the adsorption equilibrium before being filtered and measured. The test is done in triplicate. Equilibrium adsorption capacity, qe (mg/g) is measured as equation 1.

The steps were repeated for all the absorbance readings of concentration of naproxen sodium solution in OPEFB at 1 hour. The original and final concentrations of naproxen were measured, and the percentage of naproxen removal was determined using the equation (2) below:

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qe = \frac{(c_i - c_e)v}{w} \tag{1}
$$

Where:

 $Ci = Initial Diclofenac concentration (mg/L)$

 $Ce = Equilibrium Diclofenac concentration (mg/L)$

 $V =$ Volume of the Diclofenac solution (L)

 $W = Weight of the adsor bent that was used (mg)$

Removal percentage of Naproxen (%) = $\frac{c_i - c_e}{c_i} \times 100\%$ (2)

Where Ci represented as the initial concentration of the sample (mg/L) and Ce as the final concentration of the sample (mg/L).

3 Results and Discussion

3.1 Adsorbent dosage effect

Currently, there are many studies have been conducted about the applications of biochar in the removal of varieties of pollutants like pharmaceutical waste [4], removal of zinc from aqueous solution [1,2], removal of organic and inorganic pollutants from industrial wastewater [6], removal of microplastics from water [7] and many more. From here, researchers have agreed that biochar is a promising adsorbent for water treatment because of its high porosity, high total pore volume, large specific surface, strong chemical stability, and high physical hardness number [5]. Logically, the higher the amount of the adsorbent used, the higher capability of adsorbents to adsorb the pollutants. The same goes for the size of the adsorbents, where a smaller size will increase the effectiveness of the adsorption [1]. This experiment was able to prove that the amount of OPEFB biochar used to adsorb naproxen sodium is one of the elements to achieve high removal efficiency. Figure 4 is the graph of the percentage removal efficiency of naproxen sodium $(\%)$ against the concentration of naproxen sodium solution (ppm) using 2.5 g of OPEFB biochar for 0.5 hours, 1 hour and 24 hours. From the graph below, a 100 ppm concentration solution showed the highest removal efficiency of naproxen sodium solution which was 99.77% after 24 hours of experiment has been conducted. Meanwhile, a 150 ppm solution of naproxen sodium showed the lowest efficiency removal which was 98.21% for 24 hours throughout the experiment has been held but at 0.5 hours, the removal efficiency for 150 ppm is the second lowest which was 7.73%.

Fig. 4. The percentage removal efficiency of naproxen sodium (%) against the concentration of naproxen sodium solution (ppm) using 2.5 g of OPEFB biochar for 0.5 hours, 1 hour and 24 hour.

3.2 Naproxen concentration effect

Figure 5 show the equilibrium adsorption of naproxen sodium solution, qe against the concentration of naproxen sodium solution (ppm) in 1 hour using 2.5 g and 5.0 g of biochar. When using the 2.5 g of biochar, the highest equilibrium adsorption showed at the concentration of 1000 ppm which was 3.94% and the lowest value of equilibrium adsorption in the same amount of biochar was 100 ppm, which was 0.30%. Meanwhile, the lowest equilibrium adsorption recorded for 5.0 g was at 0.17% for 100 ppm and the highest value of equilibrium adsorption was at 1000 ppm, which was 1.91%.

The higher the value of equilibrium adsorption, the higher effectiveness of biochar to remove the naproxen sodium. Using different amounts of OPEFB biochar gives significant factors in removing the pharmaceutical waste in wastewater rather than using the raw untreated empty fruit bunch to absorb the pollutants. From the previous study, using raw OPEFB gives colour changes to the solution due to the lignin effects which affected the colour of the solution and decreased lightness. Unlike the OPEFB biochar, even though the naproxen sodium solution turned yellowish colour due to the decolourization, it didn't affect the concentration readings since the usage of HPLC is to detect the naproxen sodium left in the solution after the experiment.

Fig. 5. The equilibrium adsorption of naproxen sodium solution, q_e against the concentration of naproxen sodium solution (ppm) in 1 hour using 2.5 g and 5.0 g of biochar.

4 Conclusion

This study establishes the capability of using OPEFB waste that turned into biochar as the cost-efficient adsorbent for the removal of naproxen sodium. From the adsorption experiment, the results showed that the adsorbent amount and the adsorption contact time gives a significant impact on the adsorption performance of the naproxen sodium concentration by the OPEFB biochar.

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