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To cite this article: N R Nik Yusoff et al 2022 IOP Conf. Ser.: Earth Environ. Sci. **1102** 012065

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Foxtail Palm Fruits as Potential Activated Carbon for Metamifop Removal

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Abstract. The growing demand for rice as a staple food by the expanding human population forces farmers to use substantial pesticide pest control on their crops. Water pollution is a serious problem as a result of overuse of agrochemical pesticides. Nominee-M, a recently created post-emergence formulation herbicide that has been investigated, contains the active component metamifop. Herbicides that protect crops from weed infestation frequently contain this chemical. The purpose of this study was to examine the effectiveness and potential of foxtail palm fruits as a potential source of activated carbon for the elimination of metamifop. Nitric acid $(HNO₃)$ was used in the chemical process of chemical activation to create the activated carbon from the foxtail palm fruits. The effect of adsorbent dose used $(2 g, 3 g, 4 g)$ and 5 g), contact time (60 mins, 90 mins, 120 mins and 150 mins) and initial metamifop concentration (10 mg/L, 12 mg/L, 14 mg/L, 16 mg/L and 18 mg/L) toward the efficiency of the prepared activated carbon in removing metamifop was studied in this research. The highest percentage removal was 86.65%, obtained at optimized value of 3 g of activated carbon used at 60 minutes of contact time and 10 ppm of initial concentration of metamifop. The study has proven that activated carbon produce from foxtail palm fruit potentially reduce metamifop in water resources that has been contaminated.

1. Introduction

Agrochemicals are medium used for the management of agricultural ecosystem to protect crops from any diseases, pests and weeds which includes fertilizers, herbicides and pesticides. Apart from crops protection, the uses of these chemical have contributed to the efficiency of farmers while maintaining the supply of agricultural products to meet the global food supply. Despite the contribution of agrochemicals as a medium for protection of crops which also increase the work efficiency of the farmers, excessive use of the chemicals can cause diffuse water pollution. Diffuse water pollution is described as any activities which does not have any specific point of discharge [1]. Contamination of water caused by agrochemicals will affect human and aquatic species [2]. Contaminated water is not suitable for human consumption. Besides that, runoff of agrochemicals into larger water bodies can causes eutrophication, a phenomenon when a source of water is overloaded with nutrients such as nitrogen and phosphorus which initiate the growth of algae [3]. In this study, metamifop is an active

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ingredient in herbicide formulation which use to control weeds can potentially contaminate the water body and can bio-accumulates in plants or crops [4, 5]. Hence, finding an effective treatment strategy for this type of herbicide is therefore an issue. The majority of techniques have been used, including photocatalytic degradation [5,6], phytoremediation [7], zeolite [8], chemical coagulants [9, 10], and various types of absorbents [10, 11]. Some of them work well, while others require to be paired with another treatment. Due to its capacity to remove gas, dye [12, 13], and other contaminants, the adsorption technique using activated carbon has lately been used in drinking water purification and wastewater treatment. The cost production of activated carbon posed the biggest obstacles to adsorption process [14, 15]. As a result, substantial effort has been made to produce activated carbon from agricultural waste [16–18], which can subsequently help to tackle significant waste management problems [19–20]. Traditionally, coal or charcoals have been used to create activated carbon. However, because it is sustainable, producing activated carbon from renewable resources is more exciting [21]. Foxtail palm fruit, or Wodyetia bifurcata, is the agro-waste that will be utilised. In Malaysia and other nations, it is a variety of palm tree from the Arecaceae family that is frequently grown as a landscaping plant [19]. The foxtail fruits are always left to rot and are never explicitly used. However the palm kernel shell wastes have been used to remove dye such as methylene blue [22]. Therefore, generating activated carbon from foxtail fruits is hope to be transformed the non-used foxtail fruit waste into a profitable product plant [19].

2. Materials and Methods

2.1 Preparation of Activated Carbon from Foxtail Palm Fruit

The foxtail palm fruit were collected at Jeli, Kelantan Malaysia (5.7492° N, 101.8600° E). The distilled water was used to carefully clean the foxtail palm fruits to get rid of any surface impurities or debris. The sample was then dried in an oven for an entire night at 100°C before being cooled to room temperature. The dried fruit was then carbonised for two hours at 300°C in a furnace and later it was cooled to room temperature. The char was was broken up into tiny bits and then ground in a miller blender to obtain smaller portions using an octagonal agate pestle and mortar. The char was sieved through a 250 m mesh sieve. A beaker containing concentrated nitric acid with volume of 80 ml was used to soak and impregnate about 40 g of the char. The mixture was mixed and constantly stirred for 30 minutes until it became paste and left overnight in the fume hood to allow the activation. Next, the slurry was measured, put in crucibles and carbonized for 2.5 hours in a furnace at 500˚C. In order to achieve pH 7, the activated carbon was next rinsed with distilled water and heated for 3 hours at 150°C in the oven. Finally, the dried activated carbon was kept in tight bottle and located in desiccators for subsequent use.

2.2 Characterization of the Prepared Activated Carbon

The observation of the surface morphology of the foxtail palm fruit activated carbon was observed using Quanta 450 FEG Field Emission Scanning Electron Microscope (FESEM) (Quanta FEG 450; FEI Company, Hillsboro, Oregon, USA). The micrograph image of activated carbon was captured using 5000X magnification level.

2.3 Preparation of Metamifop Solution

The metamifop stock solution (1000 ppm) was prepared by dissolving 10.5 g of Nominee-M formulation (that contain active ingredient of metamifop) into 1 L of deionized water and later stored in refrigerator at 4˚C for later usage.

2.4 Adsorption Experiment on Metamifop Solution

The adsorption test was performed by mixing 50 mL of 10 ppm metamifop solution with different amount of activated carbon in Erlenmeyer flasks (250 mL) set for about 30 minutes in an incubator shaker at 200 rpm. The sample solution was withdrawn every 30 minutes, filtered with filter paper (0.45 μm Whatman) and determined using UV-Visible spectrophotometer. Experiments were performed in triplicate (n=3). The batch experiment was carried out using three variables: amount of activated carbon used $(1 \text{ g} - 5 \text{ g})$, contact time $(30 \text{ mins}, 60 \text{ mins}, 90 \text{ mins}, 120 \text{ mins}$ and 150 mins), initial concentration of metamifop used (10 ppm, 12 ppm, 14 ppm, 16 ppm and 18 ppm).

3. Results and Discussion

3.1 Characterization of activated carbon

The produced activated carbon was observed under FESEM which shown in Figure 1. The honeycomb structure on the surface of the activated carbon was visible in the micrograph and was caused by the evaporation of a chemical reagent (HNO₃) employed in the carbonization process. It was indicated that the honeycomb structure was formed due to the evaporation of $HNO₃$ during the carbonization process. This result was in line with the findings of Gan [21] which revealed that the activated carbon prepared without HNO₃ treatment had irregular pore shapes and low porous properties that was covered with impurities. While the developed honeycomb structure generates a more pores and internal surface area, it also offers high contact efficiency between the activated carbon and the flow stream of metamifop solution, that essential for an effective activated carbon and consequently could promote efficient adsorption [23].

Figure 1. FESEM photographs of the foxtail fruit activated carbon at 5000x magnification.

3.2 Effect on amount of activated carbon used

The effect on the amount of activated carbon utilized for metamifop removal was conducted. In the experiment, various amounts of 1-5 g of activated carbon were loaded in the metamifop solution. Both the initial concentration of metamifop solution and contact time was fixed at 10 ppm and 30 minutes respectively. Figure 2 shows the effect of adsorbent dose on the removal of metamifop solution.

Figure 2. Effect on the amount of activated carbon used for the removal of metamifop

The performance of the activated carbon for the removal of metamifop solution increases at the amount of 1 g, 2 g and 3 g due to large surface area and has high availability of adsorption sites. However, the adsorption efficiency of the activated carbon was slightly decreases at the amount of 4 g and 5 g used. By increasing the amount used, the percentage removal of metamifop solution was found to decrease. This result indicates that the increased in the amount of activated carbon reduces the total surface area that is available for the adsorption of metamifop solution due to overlapping or aggregation on the sites of activated carbon [24]. The percentage removal of metamifop is slightly decreases for 4 g compared to 5 g of activated carbon because the activated carbon had adhered to the wall of the conical flask which has decreased its effectiveness in removing metamifop from the solution. Only 77.99% metamifop removal was obtained when 1 g of activated carbon was applied. Meanwhile at 3 g of activated carbon used, it showed the highest percentage of metamifop removal, at 85.71%. Hence, 3 g was chosen as the optimum amount of activated carbon need to be used for the subsequent experiments.

3.3 Effect of contact time

The amount of activated carbon and the concentration of metamifop solution were fixed at 3 g and 10 ppm respectively. The effectiveness of the activated carbon for the adsorption of metamifop solution increases and improves from 30 to 60 minutes of contact time (Figure 3). The metamifop solution was rapidly removed (86.65%) by the adsorption of activated carbon at the initial contact time of 60 minutes due to the high availability of adsorption sites and strong attractive forces between the molecules of the metamifop and the adsorbent [25]. However, the adsorption of metamifop by

activated carbon become moderately decreases starting from contact time of 90 to 150 minutes. An equilibrium between the amount of metamifop adsorbed by the activated carbon and amount of metamifop that remained in the solution was not reached. This result indicates that the adsorbent sites were fully occupied by the metamifop molecules. The collision between the molecules of metamifop and the activated carbon become bigger as the contact time increases [26]. Contact time of 60 minutes was chosen as the optimum contact time for the subsequent experiment.

Figure 3. Effect of contact time on the removal of metamifop by activated carbon

3.4 Effect on the initial concentration of metamifop used

The effect of the initial metamifop concentration on the adsorption efficiency of activated carbon from foxtail palm fruits for the removal of metamifop was conducted at different initial concentration of 10, 12, 14, 16 and 18 ppm Figure 4). The amount of activated carbon used and the contact time were fixed at 3g and 60 minutes respectively. As the initial concentration of the metamifop solution rises, the effectiveness of the activated carbon for the adsorption of the solution diminishes. Due to the activated carbon's larger surface area and greater availability of adsorption sites, the metamifop molecules were efficiently adsorbed at the lowest concentration which was 10 ppm [25]. The accessible active sites were thus completely occupied as a result of the interaction between the molecules of metamifop and the adsorbent. The adsorption of metamifop by the activated carbon was constrained at the highest concentrations of metamifop, which were 12 ppm, 14 ppm, 16 ppm, and 18 ppm [25].

The highest percentage of metamifop elimination was observed at an initial concentration of 10 ppm, at 86.65%, while the lowest percentage was recorded at an initial concentration of 18 ppm, at 46.43%.

As a result it was decided that 10 ppm was selected as the optimum initial concentration of metamifop that would be effectively removed by activated carbon.

Figure 4. Effect of initial metamifop concentration on the removal of metamifop by activated carbon

4. Conclusion

According to the study, metamifop was removed by activated carbon that chemically activated by HNO3. The effect of adsorbent dose, contact time and initial metamifop concentration toward the efficiency of prepared activated carbon in removing metamifop was conducted. From the study, the optimum amount of activated carbon use, contact time and initial metamifop concentration were obtained at 3 g, 60 minutes and 10 ppm respectively. This resulted in the maximum percentage of metamifop removal, which was 86.65%. Thus, the activated carbon produced from foxtail palm fruits can therefore be potentially commercialized for the treatment of metamifop-contaminated water.

Acknowledgement

We would like to express our gratitude to Universiti Malaysia Kelantan for providing technical assistance and lab resources.

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