Journal of Analytical and Applied Pyrolysis 110 (2014) 172–180

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

Preparation of mesoporous activated carbon from coconut frond for the adsorption of carbofuran insecticide

V.O. Njoku[a,b], M. Azharul Islam[a,c], M. Asif[d], B.H. Hameed[a,*]

[a] *School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia*
[b] *Department of Chemistry, Faculty of Science, Imo State University, P.M.B. 2000 Owerri, Nigeria*
[c] *Forestry and Wood Technology Discipline, Khulna University, Khulna 9208, Bangladesh*
[d] *Chemical Engineering Department, College of Engineering, King Saud University, PO Box 800, Riyadh 11421, Saudi Arabia*

ARTICLE INFO

Article history:
Received 26 June 2014
Accepted 16 August 2014
Available online 16 September 2014

Keywords:
Carbofuran
Coconut frond activated carbon
H_3PO_4
Isotherm
Kinetic

ABSTRACT

This paper provides a scientific research about the novel activated carbon produced from coconut frond for the removal of toxic pesticide carbofuran. The coconut frond was chemically modified by H_3PO_4 with an impregnation ratio of 1:1 and later activated at 500 °C for 2 h. The produced coconut frond activated carbon (CFAC) were characterized by surface area measurement, Fourier transform infrared spectroscopy and scanning electron microscopy. The CFAC had a BET surface area of 483 m^2/g and a cumulative pore volume of 0.21 cm^3/g. Over 80% of 250 mg/L carbofuran was adsorbed within 4 h at 30 °C and the adsorption was not dependent on pH due to the nonionic nature of carbofuran. The adsorption kinetic was best represented by the pseudo-second-order model. The adsorption equilibrium data fitted best to the nonlinear Freundlich isotherm model. Thermodynamic parameters obtained showed that the adsorption was spontaneous and endothermic in nature. Adsorption mechanisms were analyzed using intraparticle diffusion and Boyd kinetic models, and film diffusion was confirmed as the rate-controlling step. These results indicate that CFAC is an efficient adsorbent for the removal of the nonionic pesticide, carbofuran from aqueous solution.

1. Introduction

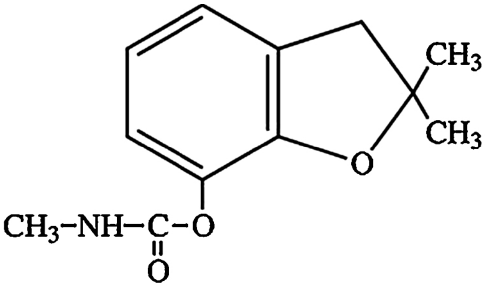
Malaysia is presently one of the world's dominant exporters of palm oil, natural rubber and cocoa. However, rice, pepper, pineapple and tobacco are also adding extra value to the Malaysian agro-economy mainly the agro-food based industry. In order to meet the present demand of the growing population as well as realize the desired sound economy, the flow of agricultural production should be in a sustained manner by selecting high yield varieties of crops (HYV), improvised techniques and sound agricultural policies. As a result, Malaysian agriculture turned into a monoculture technology with HYVs which needed very effective plant protection strategies. The major challenge of monoculture is that if a crop is infested by a certain pest and disease, then it will spread in epidemic form. Besides, as a tropical country, the Malaysian crops are always susceptible to various fungi and insect invasion which hamper the desired crops production. Therefore, application of pesticides is adopted to ensure the control of disease-borne pests in this regard. Almost all the pesticides used in Malaysia are applied in the rubber, oil palm, and rice sectors of agriculture [1]. However, indiscriminate and intensive use of pesticides may cause several environmental problems through contamination of surface and ground water. Besides, reckless disposal of empty containers and accidental or intentional discharge of pesticides may perhaps contaminate the adjacent water bodies. The toxic effect of these chemicals brings myriad sufferings to the non target population including aquatic organisms and humans.

Carbofuran is an insecticide and nematicide used in the rice fields for the control of rodents and in the oil palm plantations for the control of the rhinoceros beetle in Malaysia [2]. It is moderately soluble in water, non-volatile and, based on its chemical properties, has high potential for groundwater contamination [3,4]. It is not persistent in soil but one study by Farahani et al. [2] stated that carbofuran is more stable in ground water than in other types of water in Malaysia due to the low pH value. The mammalian toxicity of carbofuran is high but bioaccumulation potential is less. Carbofuran is an endocrine disruptor and a probable reproduction/development intoxicant [3]. It is highly toxic to birds and honeybees whilst having a moderate to high toxicity to most aquatic organisms including sediment dwelling organisms. The acute toxicity (LC50) data on

---

* Corresponding author: Tel.: +604 5996422; fax: +6045941013.
E-mail address: chbassim@usm.my (B.H. Hameed).

http://dx.doi.org/10.1016/j.jaap.2014.08.020
0165-2370/



Scheme 1. Chemical structure of carbofuran.

Malaysian aquatic catfish (*Clariusbatrachus*) was found to be 5 mg/L at 96 h suggesting moderate toxicity [5]. It is also moderately toxic to earthworms. The maximum allowable limit for carbofuran in drinking water is 0.09 mg/L [6]. Therefore, it is a great challenge to remove this toxic element from wastewater. Utilization of activated carbon (AC) by adsorption process is a very popular and effective way to deal with these toxic and hazardous organic micropollutants from wastewater [7–11]. However, the performance of activated carbon depends on the nature of precursor, activation process as well as activation agent [12]. Recently, due to the high cost of AC and its regeneration, economically less important but locally available and renewable agricultural waste materials are being reported as activated carbon precursors [13–17].

Coconut is the third most important industrial crop in Malaysia in terms of cultivated area after oil palm and rubber [18,19]. Coconut is considered as a versatile plant species. Other than food values, coconut shell and husk are very promising sources of valuable activated carbon. In Malaysia, about 151,000 ha of land were being used for coconut plantation in the year 2001 [20] but this is gradually decreasing every year due to competition with oil palm for land. Recently, a coconut industry revitalizing plan (2008–2015) was initiated to replant and rehabilitate the coconut plantation area [21]. Every year, huge quantities of fronds are produced by natural pruning and silvicultural practice and these usually remain as waste in the forest floor which aggravates fungi and pest infestation.

Therefore, this study was attempted to produce activated carbon from coconut frond as precursor for the first time. Literature review also shows that no research has been carried out on the removal of carbofuran by coconut frond activated carbon as well.

2. Materials and methods

2.1. Adsorbate

Carbofuran (2,3-dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate, chemical formula: $C_{12}H_{15}NO_3$, molecular weight: 221.3 mg/mol, solubility in water 322 mg/L at 20 °C) [3], with purity of 99.9% supplied by Sigma-Aldrich (M) Sdn. Bhd., Malaysia was used as an adsorbate. The pH of the solutions was adjusted to desired values by adding 0.1 M HCl or 0.1 M NaOH solutions. All other chemicals used in this study were analytical grade and were used without further purification. The structure of carbofuran is shown in Scheme 1.

2.2. Preparation of activated carbon

Coconut frond were collected locally and cut into small pieces, repeatedly washed with distilled water until removal of dirt from it surface and then dried in an oven at 70 °C. The dried samples were ground and sieved to particle size ranges from 500 to 710 μm and further dried in the oven. The sample was then soaked in orthophosphoric acid (H_3PO_4) with an impregnation ratio of 1:1 (w/w) for 24 h and dehydrated in an oven overnight at 105 °C. The resultant sample was activated in a temperature programmable stainless steel vertical electric tubular furnace at 500 °C with constant heating rate of 10 °C/min, under purified nitrogen (99.99%) with flow rate of 150 cm^3/min for 2 h. The AC produced was cooled to room temperature and washed with 0.1 M HCl (to remove ashes that blocks the pores) and successively with hot distilled water repeatedly until the pH of the washing solution reached 6–7. The final product was dried in an oven at 105 °C for 24 h and kept in an airtight container for further use.

2.3. Characterization of activated carbon

The surface area and porosity properties of CFAC were determined by nitrogen (N_2) adsorption–desorption at −196 °C (77 K) with an automated gas sorption system (Micromeritics, Model ASAP 2020, USA). The surface functional groups of CFAC were determined using Fourier transform infrared (FT-IR) spectroscopy (Perkin Elmer, Model 2000 FT-IR, USA). The surface morphology of CFAC was examined using a scanning electron microscope (SEM, Zeiss Supra 35 VP, Germany). The point-of-zero-charge (pH_{PZC}) of CFAC surface was determined by using the solid addition method [22]. Absorbance measurements were done using a double beam UV/visible spectrophotometer (Shimadzu, Model UV 1700, Japan) at 276 nm.

2.4. Adsorption experiments

Batch adsorption tests were performed by mixing 0.20 g of CFAC adsorbent with 200 mL of carbofuran solutions with initial concentrations of 25–250 mg/L in a set of Erlenmeyer flasks (250 mL). Then each flask was covered with glass stopper and the flasks were placed in an isothermal water-bath shaker at different controlled temperature (30–50 °C) with agitation speed of 120 rpm to reach equilibrium [23]. The concentrations of carbofuran in the solution before and after adsorption were determined using a double beam UV–vis spectrophotometer (Shimadzu, UV-1700, Japan) at its maximum wavelength of 276 nm. The removal% was calculated as:

$$\text{removal\%} = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{1}$$

The quantity adsorbed at equilibrium, q_e (mg/g), was calculated by:

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{2}$$

The quantity adsorbed at time t, q_t (mg/g), was calculated using the following equation:

$$q_t = \frac{(C_0 - C_t)V}{W} \tag{3}$$

whereC_0, C_e and C_t (mg/L) are the concentrations of carbofuran at initial, at equilibrium and at time t (h), respectively. V (L) is the volume of the solution and W (g) is the mass of dry adsorbent used.

3. Results and discussion

3.1. Characterization of activated carbon

The N_2 adsorption–desorption isotherm curve at 77 K of CFAC is presented in Fig. 1a. According to the isotherm classification based on shape by Sing et al. [24], the isotherm found in this study can be considered as Type IV, which exhibits a limited uptake at high relative pressures (P/P_0) but at low pressure monolayer coverage may occur followed by further or multilayer coverage. In addition, a marked hysteresis loop was observed (Fig. 1a) indicating inherent mesoporosity of the material. The Brunauer–Emmett–Teller