NEW CARBON MATERIALS
Volume 29, Issue 1, Feb 2014
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com
ScienceDirect

Cite this article as: New Carbon Materials, 2014, 29(1):47–54.

RESEARCH PAPER

Rice straw-derived activated carbons for the removal of carbofuran from an aqueous solution

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Abstract: Activated carbon was prepared from rice straw by carbonization and KOH activation, and was used as an adsorbent for the removal of a kind of pesticide, carbofuran (2,3-dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate) from aqueous solution. The effects of the initial carbofuran concentration, contact time, temperature and pH, on its adsorption capacity and kinetics were studied using a batch method. The surface area and average pore diameter of the activated carbon were 1304.8 m^2/g and 2.39 nm, respectively. The maximum adsorption capacity of the activated carbon (296.52 mg/g) for carbofuran was found to occur at 90 min, 30 °C and 200 mg/L initial carbofuran concentration with an adsorbent loading of 100 mg/L. Equilibrium adsorption isotherms were fitted better by the Langmuir model than the Freundlich and Temkin models. The adsorption follows a pseudo-second-order kinetics model.

Key Words: Rice straw; Carbofuran; Activated carbon; Adsorption isotherm; Kinetics

1 Introduction

Chemical pesticides are frequently applied in agriculture to ensure good harvests. However, the problem of chemical pesticides in the environment has become a social issue as these contaminants have frequently been detected in various water sources and in soil in recent years[1]. Carbofuran (2,3-dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate), a derivate of carbamate pesticides, is an insecticide and nematicide widely used on soybeans, rice, potatoes, fruits and vegetables. The heavy use of carbofuran has become an environmental concern because it is toxic, carcinogenic and recalcitrant. In 2008, Taiwan used approximately 1803 tons of carbofuran in agriculture, especially on rice fields. The half-life of carbofuran has been reported to be approximately 40 d[2], and the drinking water quality standard set by the World Health Organization is 3 μg/L. Therefore, it is important to develop an effective technology for the rapid removal of carbofuran from water.

The conventional techniques for treating pesticide-containing wastewater are the Fenton method with coagulation[3], photo- and electro-Fenton method[4], combined ultrasound and Fenton method[5], oxidants and photo[6], biological degradation[7,8] and adsorption[9,10]. Among the numerous clean-up techniques, adsorption with activated carbon is an ecofriendly method that is widely used for the removal of pesticides, but activated carbon is still considered to be an expensive adsorbent. Recently, various low-cost adsorbents derived from agricultural waste and natural materials have been investigated for pollutant removal from aqueous solutions. These adsorbents include sunflower oil cake[11], sugar beet bagasse[12], bamboo[13,14], coconut shells[15] and chestnut shells[16].

Rice is a widely grown crop in Asia, and open-field burning of rice straw is commonly practiced in the region when there is limited time to prepare a field for the next crop. However, open-field burning of crop residues is an uncontrolled combustion process during which air pollutants are emitted into atmosphere. These air pollutants have significant toxicological properties and are potential carcinogens[17]. In the present study, rice straw, an agricultural waste available in large quantities in Asia, was utilized as a precursor for low-cost adsorbents to remove carbofuran from aqueous solution by adsorption. We used two-stage method to convert rice straw into high-surface-area activated carbon. The adsorption capacity of the activated carbon from rice straw has not yet been explored for the removal of carbofuran from water. Batch adsorption was used to evaluate the maximum

Received date: 05 April 2013; **Revised date:** 23 November 2013
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DOI: 10.1016/S1872-5805(14)60125-6

adsorption capacity of the activated carbons. The effects of the initial carbofuran concentration, contact time, temperature and pH on carbofuran adsorption capacity and kinetics were studied. Adsorption isotherms and kinetic parameters were also calculated and discussed. This method is not only effective for the removal of carbofuran from environmental water, but it also helps to reduce air pollution by preventing open-field burning.

2 Experimental

2.1 Raw material

The straw from 5-month-old japonica rice (*Oryza sativa* L.) plants of the Tainung 67 variety was obtained from an experimental farm located on the Academia Sinica campus, Taipei, China.

2.2 Activated carbon preparation

We placed the rice straw in an ashing furnace and dried it at 110 °C for 12 h. One hundred grams of oven-dried rice straw was carbonized in the first stage. Next, 100 g of rice straw was put into a furnace, and the temperature was increased to 280 °C at a heating rate of 5 °C /min for 2 h to vaporize all organic compounds. Then, the temperature was further increased to 450 °C at a heating rate of 10 °C /min for 2 h to carbonize the rice straw. When the rice straw char had cooled from 450 °C to room temperature, we mixed the rice straw char with potassium hydroxide (KOH) powder in a mass ratio of 1: 2 and then added de-ionized water to dissolve the KOH and make a 4 mol/L KOH solution.

After 30 min, the mixture was transferred to an ashing furnace; the temperature was increased to 450 °C at a heating rate of 10 °C /min for 2 h and then increased again to 850 °C at a heating rate of 10 °C /min for 3 h. This was the second stage of the heating process known as the activation process, which transforms rice straw char into activated carbon. Once the activated carbon had returned to room temperature, we washed it with a large amount of de-ionized water to reduce its alkalinity (pH~10) to close to neutral (pH value~7). Finally, we dried the activated carbon product at 110 °C for 12 h. The adsorbents were stored in separate vacuum desiccators until they were needed.

2.3 Activated carbon characterization

The specific surface area of the activated carbon was determined from a nitrogen (N_2) adsorption-desorption isotherm. A Micromeritics ASAP 2010 instrument was used to determine this parameter, and the average pore diameter was calculated from the adsorption branch of the N_2 isotherm. The morphological structure of the activated carbons was determined by using an FEI Quanta 200 scanning electron microscope (SEM). Elemental analysis of the samples was performed using an Elementar Vario EL III elemental analyzer (Germany). Fourier transform infrared spectroscopic (NEXUS470, ThermoNicolet) analysis was used to determine the surface functional groups of the native and carbofuran-exposed activated carbons, and spectra were recorded from 4000 to 500 cm^{-1}.

2.4 Adsorption equilibrium and kinetic studies

A fixed amount of activated carbon (10 mg) was added to one of a set of 250 mL Erlenmeyer flasks containing 100 mL of carbofuran solution at different initial concentrations (25-200 mg/L) without pH adjustment. The flasks were agitated in an isothermal water bath shaker at 180 r/min and 30 °C for 90 min until equilibrium was reached. The solution was then filtered with a Pall syringe filter (0.2 μm PTFE membrane). Subsequently, the residual carbofuran concentration in the filtrate was analyzed using high-performance liquid chromatography (HPLC, DIONEX, UltiMate 300) at a wavelength of 210 nm. The mobile phase for the HPLC analysis was 40:60 (v/v) acetonitrile and deionized water. The amount of adsorption at equilibrium, q_e (mg/g), was calculated as

$$q_e = \frac{(C_o - C_e)\ V}{W} \tag{1}$$

where C_o and C_e (mg/L) are the initial and equilibrium liquid-phase concentrations of carbofuran, respectively, V (L) is the volume of the solution and W (g) is the mass of the activated carbon used.

The amount of adsorption at time t, q_t (mg/g), was calculated as

$$q_t = \frac{(C_o - C_t)\ V}{W} \tag{2}$$

2.5 Effect of initial concentration and contact time

Ten-milligram samples of activated carbon were added to 100 mL of carbofuran solution at initial concentrations of 25, 50, 100, 150 and 200 mg/L, and the experiments were conducted at 30 °C for 90 min with an adsorbent dose of 100 mg/L.

2.6 Effect of temperature

The effect of temperature on carbofuran adsorption was determined in flasks sealed with Teflon-lined caps. Ten-milligram samples of activated carbon were added to 100 mL of 13 mg/L carbofuran aqueous solution. The experiment was conducted at 20, 30 or 40 °C for 90 min with an adsorbent dose of 100 mg/L.

2.7 Effect of the initial pH value of the carbofuran solution

The pH value of the solution was varied from 4.46 to 12.35, while the amount of activated carbon (10 mg), the volume (100 mL), the initial concentration of the solution (20 mg/L), the temperature (30 °C) and the shaker speed (180 r/min) were kept constant. The pH of the solution was