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Adsorption Studies on the Removal of Pesticides (Carbofuran) using Activated Carbon from Rice Straw Agricultural Waste

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***Abstract*—**In this study, we used a two-stage process and potassium hydroxide (KOH) to transform waste biomass (rice straw) into activated carbon and then evaluated the adsorption capacity of the waste for removing carbofuran from an aqueous solution. Activated carbon was fast and effective for the removal of carbofuran because of its high surface area. The native and carbofuran-loaded adsorbents were characterized by elemental analysis. Different adsorption parameters, such as the initial carbofuran concentration, contact time, temperature and pH for carbofuran adsorption, were studied using a batch system. This study demonstrates that rice straw can be very effective in the adsorption of carbofuran from bodies of water.

***Keywords*—**Rice straw, Carbofuran, Activated carbon

I. INTRODUCTION

CHEMICAL pesticides are frequently applied in agricultural to ensure good harvests. However, the problem of chemical pesticides in the environment has become a social issue as these contaminants were frequently detected in different water sources, rivers and soil in recent years [1]. Carbofuran (2,3-dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate), one of the derivates of the carbamate pesticides, is a widely used insecticide and nematicide on soybeans, rice, potatoes, fruit and vegetable crops. The use of carbofuran has become of environmental concern not only because its heavy rate of use but also because it is toxic, carcinogenic and recalcitrant. In 2008, Taiwan used Carbofuran about 1,803 ton in agriculture especially in rice fields. It was reported that the halflife of Carbofuran is approximately 40 days [2] and the drinking water quality standard is 3 μg/L for Carbofuran by the World Health Organization (WHO). Therefore, it is important for developing the effective technology to rapid remove Carbofuran from water body.

The conventional methods for treating pesticides containing wastewaters are Fenton with coagulation [3], photo and electro-Fenton [4], combined ultrasound and Fenton [5], Oxidants and photo [6], biological degradation [7-8] and adsorption [9-10]. Among numerous clean-up techniques, adsorption technique with activated carbon is ecofriendly method and widely used for the removal of pesticides, but it is still considered expensive adsorbent. Recently, various low-cost adsorbents derived from agricultural waste or natural materials, have been investigated for pollutant removal from aqueous solutions. Some of these adsorbents are sunflower oil cake [11], sugar beet bagasse [12], bamboo[13-14], coconut shell [15] and chestnut shells [16]. Rice is a widely grown crop in Asia and the open field burning of rice straw is commonly practiced in the region when there is a short duration to prepare the field for the next crop. However, it has been observed that open field burning of crop residues is a process of uncontrolled combustion during which air pollutants are emitted into the atmosphere. And these air pollutants have significant toxicological properties and are notably potential carcinogens [17]. In this study, rice straw, an agricultural waste available in large quantity in Asia, was utilized as low-cost adsorbent to remove Carbofuran from aqueous solution by adsorption. We used two-stage processes to make rice straw to activated carbon with high surface area. The adsorption capacity of the rice straw carbonaceous adsorbents has not yet been explored for Carbofuran removal from water. Batch adsorption process has been used to evaluate the maximum adsorption capacity of activated carbon produced from rice straw. The effects of initial Carbofuran concentration, contact time, temperature and pH on Carbofuran adsorption were studied. Adsorption isotherms and kinetics parameters were also calculated and discussed. The method not only can solve air pollutants issue but also can removal Carbofuran from environmental water.

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II. MATERIALS AND METHODS

A. Raw material

The straw from the 5 month-old plants of a japonica rice (*Oryza sativa* L.) variety Tainung 67 were obtained from the experimental farm (25° 02' 32.79"N, 121° 36' 47.40"E with 18 m of elevation) located in Academia Sinica campus, Taipei, Taiwan. The rice plants were transplanted to the field at the first week of March, 2009 and got heading (flowering) at the first week of June. The straw (leaves and stems) were harvested after the seeds were harvested at late July. They were washed and dried in sunlight before use.

B. Activated carbon preparation

As shown in Fig. 1, we used a two-stage process and potassium hydroxide (KOH) to promote the formation of activated carbon from charcoal. The adsorbents were stored in separate vacuum desiccators until they were needed.

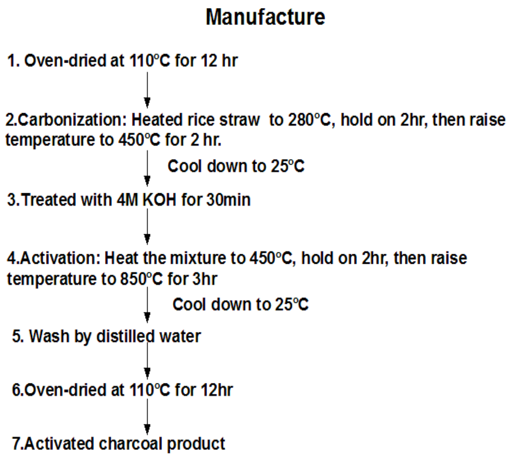

Fig. 1. Procedure for the preparation of activated carbon

C. Activated carbon characterization

Specific surface area

The specific surface area of activated carbon was determined from adsorption- desorption isotherm of nitrogen gas (N_2). The Micromeritics ASAP 2010 was used for this parameter and the average pore diameter was calculated from the adsorption branch of the N_2 isotherm.

Element analysis (EA)

Elemental analysis of samples was carried out by using Elementar Vario EL III (Germany).

D. Effect of initial concentration and contact time

10 mg sample of activated carbon was added to each 100mL volume of Carbofuran solution with initial concentrations of 25, 50, 100, 150 and 200 mg/L and the experiments were carried out at 30 °C for 90min.

E. Effect of temperature

The effect of temperature on Carbofuran adsorption was carried out in flasks sealed with Teflon lined caps. 10 mg sample of activated carbon was added to each 100mL volume of 13 mg/L Carbofuran aqueous solution. The experiments were carried out at 20 °C, 30 °C and 40 °C for 90 min.

F. Effect of initial pH of the Carbofuran solution

The pH of the solution was varied from 4.46 to 12.35, while the amount of adsorbent (10 mg), volume of solution (100 mL), initial concentration of solution (20 mg/L), temperature (30 °C) and shaker speed (180 rpm) were kept as constants. The solution pH was adjusted by using the diluted 0.1 M HCl and 0.1 N NaOH.

III. Results and Discussion

The BET surface area and average pore diameter of the adsorbent were found to be 1304.8 m^2/g and 23.9 Å, respectively. Table 1 shows the elemental content of raw rice straw and activated carbon for before, after adsorption. The major elements of materials such as C, H, N, and S were examined. Activated carbon prepared from rice straw show higher carbon content (41.925%) compared to the raw material (36.578%) and high content of carbon element (71.346%) was obtained after adsorption. This indicated that some of Carbofuran were adsorbed on the activated carbon surface.

TABLE I
ELEMENTAL CONTENT OF RAW RICE STRAW AND ACTIVATED CARBON FOR BEFORE AND AFTER ADSORPTION

	Elements (%)			
	C	H	N	S
Raw rice straw	36.578	5.521	0.851	0.016
Before Adsorption	41.925	3.542	1.427	1.146
After Adsorption	71.346	4.507	1.645	0.806

The uptake of Carbofuran molecules by the adsorbents, and the time required for establishment of equilibrium suggest the effectiveness of the materials for Carbofuran treatment. In order to determine the equilibrium time for maximum Carbofuran uptake, an initial concentration and contact time study was carried out. Effect of initial concentration and time on Carbofuran removal by activated carbon was investigated with varying initial concentrations (25, 50, 100, 150 and 200 mg/L), adsorbent dose (100 mg/L), stirring speed (180 rpm), temperature (30 °C) constant and different contact times (10, 20, 30, 40, 50, 60 and 90 min). Fig. 2 shows the adsorption uptake versus the adsorption time at various initial Carbofuran concentrations. The removal of Carbofuran by activated carbon increased with time and then reached equilibrium at about 90 min. When the initial BPA concentration increased from 25 to 200 mg/L, the loading capacity of activated carbon increased from 135.99 to 296.52 mg/g and the percentage removal decreased from 59 to 15%. Increasing Carbofuran concentration increased adsorption capacity for adsorbent, could be provided the necessary driving force to overcome the resistances to the mass transfer of Carbofuran between the aqueous and solid phases [18]. It is clear that the removal of Carbofuran depends on the concentration of the Carbofuran. Further, the removal was rapid in early stages and finally attained almost constant value for longer contact time. Obviously, the initial high adsorption rate is due to the abundance of free binding sites. Additionally, at low concentration, the ratio of available surface to the initial Carbofuran concentration is larger, so the removal is higher. However, in case of higher concentrations, this ratio is low; hence the Carbofuran removal percentage is lesser.

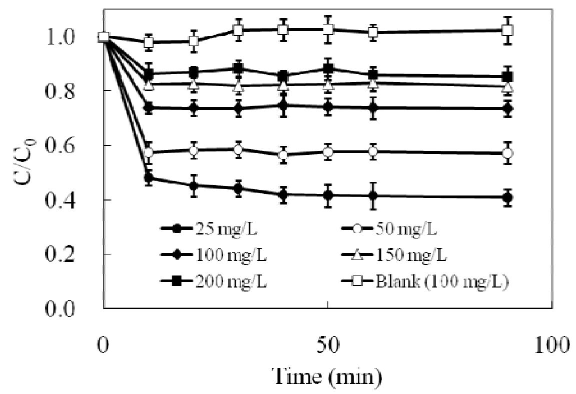

Fig. 2 The variation of Carbofuran concentration with adsorption time at various initial Carbofuran concentrations

Temperature has a direct influence on the process. The adsorption experiments were conducted at 20 °C, 30 °C and 40 °C with constant Carbofuran concentration (13 mg/L), adsorbent dose (100 mg/L) and contact time (90 min). It was observed that, adsorption capacity of activated carbon decreased from 62.97 to 40.13 mg/g with increasing temperature from 20 °C to 40 °C (Fig. 3). Gupta et al. have reported that this may be due to a tendency for the target molecules to escape from the solid phase to the bulk phase with an increase in temperature of the solution [19]. A similar observation was also reported in the study on the sorption of acid dye on activated clay and activated carbon [20].

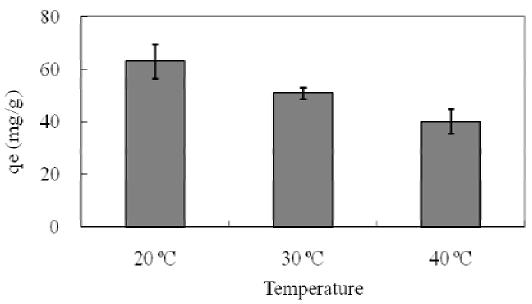

Fig. 3 Effect of different temperatures of 13 mg/L Carbofuran solutions

It is well known that pH of the solution is a critical factor in adsorption from solution [21]. The variations of the pH not only change carbon surface properties, but this parameter can also affect the state of the ionic species in solution. In order to determine the adsorption behavior of the Carbofuran, experiments were made in the initial pH range between 4.46 and 12.35, at a contact time of 90 min with constant Carbofuran concentration (20 mg/L) and adsorbent dose (100 mg/L). Adsorption capacity of adsorbents was found to be pH-dependent as shown in Fig. 4. It decreased from 128.52 to 66.92 mg/g for an increase in pH from 4.46 to 12.35. The pH dependence of adsorption process can largely be related to the type and ionic state of functional groups present on the adsorbents and compound speciation in solution. At low pH (acidic) of the solution the carbon surface is predominantly positively charged, whereas at strongly basic pH, negative charges appear on the surface, due to the dissociation of the functional groups (carbonyl, hydroxyl, etc.). This results in a less positively or more negatively charged carbon surface at higher pH than at lower pH [22]. Furthermore, it suggests a weaker interaction of activated carbon surface with deprotonated Carbofuran than with its neutral molecular form.

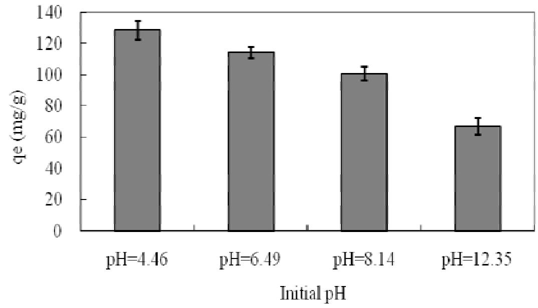

Fig. 4 Effect of different initial pH of 20 mg/L Carbofuran solutions at 30°C

Table II lists a comparison of maximum adsorption capacity of Carbofuran onto various adsorbents. Rice straw is significantly higher than all of other adsorbents developed in the recent past and have a relatively large adsorption capacity of 296.52 mg/g. Accordingly, it could be considered a promising material for the removal Carbofuran from aqueous solution.

TABLE II
COMPARISON OF ADSORPTION CAPACITIES OF DIFFERENT ADSORBENTS FOR CARBOFURAN

Adsorbent	Adsorption capacity (mg/g)	Reference
Rice straw	296.52	This study
Waste slurry	208.3	[22]
Banana stalks	147.9	[23]
Commercial activated carbon	99.4	[24]
Commercial activated carbon	96.15	[25]
Blast furnace sludge	23.0	[22]
Blast furnace dust	13.0	[22]
Bentonite	0.00226	[24]
Blast furnace slag	Negligible	[22]

IV. CONCLUSION

The present study revealed the potential of rice straw, an agricultural waste material, to be a low-cost adsorbent for removing Carbofuran from aqueous solutions. The results demonstrated that Carbofuran adsorption by NaOH treated rice straw adsorbents depends on initial Carbofuran concentration, contact time, temperature and pH. Adsorption capacity of Carbofuran increased with increase in Carbofuran concentration but decreased with increase in pH and temperature. The maximum Carbofuran adsorption capacity was 296.52 mg/g. It may be concluded that easy availability and suitability for production of carbonaceous adsorbents from rice straw biomass makes it one of the materials that can be used for removal of Carbofuran from aqueous medium.

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