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ADSORPTION OF CARBOFURAN INSECTICIDE FROM AQUEOUS SOLUTION USING COMMERCIAL ACTIVATED CARBON

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ABSTRACT

The adsorption characteristics of carbofuran on commercial activated carbon (CAC-F200) from aqueous solution were evaluated. Batch adsorption processes were conducted to study the effects of various parameters such as initial concentration, agitation time and solution pH on carbofuran adsorption. Adsorption capacity was found to increase with increase in initial concentration and agitation time, while acidic pH was more favorable for the adsorption of carbofuran. Equilibrium data were analyzed by the Langmuir, Freundlich and Temkin isotherm models. The equilibrium data were best represented by the Langmuir isotherm, yielding maximum monolayer adsorption capacity of 97.1 mg/g at 30^{o}C. The adsorption kinetics was found to follow the pseudo second order kinetic model.

Key words: Carbofuran, Comercial activated carbon, Adsorption isotherm, Equilibrium, Kinetics.

INTRODUCTION

Increasing use of pesticides in agriculture, forestry and domestic activities for controlling pests is polluting our water resources day by day. The leaching run-off from agricultural and forest lands; deposition from aerial applications and discharge of industrial wastewater are responsible for this water contamination[1]. The toxicity of pesticides and their degradation products is making these chemical substances a potential hazard by contaminating our environment[2].

Carbofuran insecticide, it is widely used for the control of soil dwelling and foliar feeding insects including wireworms, white grubs, weevils, stem borers, aphids and several other insects The maximum acceptable concentration (MAC) for carbofuran in drinking water is 0.09 mg/L (90 μg/L). Carbofuran is degraded in water by hydrolysis, microbial decomposition and photolysis. In the soil, it is degraded by hydrolysis, microbial action and

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to a lesser extent, photodecomposition. Carbofuran may be effectively removed from drinking water using activated carbon adsorption[3].

Adsorption is one of the most frequently applied methods for removal of pesticides from aqueous solutions because of its efficiency, capacity and applicability on a large scale. The most commonly used adsorbent in adsorption processes is activated carbon.

The purpose of this work was to evaluate the adsorption potential of commercial activated carbon for carbofuran. The equilibrium and kinetic data of the adsorption process were then studied to understand the adsorption mechanism of carbofuran molecules onto activated carbon.

EXPEREMENTAL

Adsorbate and adsorbent

Comercial activated carbon F200 (CAC-F200) was obtained from Calgon, US. Technical grade carbofuran ($C_{12}H_{15}NO_3$) of 99.9% purity, molecular weight (221.3 g/mol) was used as an adsorbate. Deionized water was used to prepare all the solutions and reagents.

Batch equilibrium studies

Adsorption tests were performed in a set of Erlenmeyer flasks (250 mL) where 200 mL of carbofuran solutions with initial concentrations of 25-250 mg/L were prepared. An amount of 0.20 g of the CAC-F200 was added into each flask covered with glass stopper and the flasks were then placed in an isothermal water-bath shaker at constant temperature 30^{o}C with agitation speed of 120 rpm to reach equilibrium. All samples were filtered prior to analysis in order to minimize interference of the carbon fines with the analysis. Each batch of the experiment was duplicated under identical conditions. 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 amount of adsorption at equilibrium, q_e (mg/g), was calculated by:

$$q_e = \frac{(C_o - C_e)V}{W} \quad \text{...(1)}$$

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

Adsorption isotherm

Three isotherm models (Langmuir, Freundlich and Temkin) were used to test the fitting of the equilibrium data. The linear form of the Langmuir[4] Model is -

$$C_e/q_e = C_e/q_m + 1/K_a q_m \qquad ...(2)$$

Where C_e (mg/L) is the equilibrium concentration; q_e (mg/g) the amount of carbofuran adsorbed at equilibrium; q_m the adsorption for complete monolayer (mg/g); K_a (L/mg) is the adsorption equilibrium constant. The linear form of Freundlich[5] isotherm however is -

$$\ln q_e = \ln K_F + (1/n) \ln C_e \qquad ...(3)$$

The constants K_F (mg/g(l/mg)$^{1/n}$) and $1/n$ of the Freundlich model are the constants indicative of the relative adsorption capacity of the adsorbent and the intensity of the adsorption, respectively. The Timken isotherm[6] has been used in the form given below.

$$q_e = B \ln A + B \ln C_e \qquad ...(4)$$

Where B = RT/b, b is the Temkin constant related to heat of sorption (J/mol), A is the Temkin isotherm constant (L/g), R the gas constant (8.314 J/mol K) and T the absolute temperature (K).

Effect of carbofuran solution pH

The effect of solution pH on the carbofuran removal was examined by varying the initial pH of the solutions from pH 2 to 12 using eleven separate batches of Erlenmeyer flasks (250 mL) simultaneously at the same concentration. The pH was adjusted using 0.1M HCl and/or 0.1M sodium hydroxide (NaOH) and was measured using pH meter.

Kinetic studies

Adsorption tests were performed in a set of Erlenmeyer flasks (250 mL) where 200 mL each of carbofuran solution with initial concentration of 25-250 mg/L were prepared. An amount of 0.20 g of the CAC was added into each flask covered with glass stopper and the flasks were then placed in an isothermal water-bath shaker at constant temperature 30^{o}C with agitation speed of 120 rpm. The aqueous samples were withdrawn at preset time interval and the concentration of carbofuran was determined. The amount of adsorption at time t, that is q_t (mg/g), was calculated by:

$$q_t = \frac{(C_o - C_t)V}{W} \qquad ...(5)$$

Where C_t (mg/L) is the concentration of carbofuran at time t (h). The rate constants of the adsorption were determined from the pseudo first order and pseudo second order equations. For the pseudo first order, the Lagergren[7] expression given below was used -

$$\log (q_e - q_t) = \log q_e - k_1 t/2.303 \qquad ...(6)$$

Where q_e and q_t (mg/g) are the amounts of carbofuran adsorbed at equilibrium and at time t (h), respectively and k_1(1/h) is the rate constant of adsorption.

The linear form of the pseudo second order reaction[8,9] can be given by:

$$t/q_t = 1/k_2 q_e^2 + 1/q_e^t \qquad ...(7)$$

Where the equilibrium adsorption capacity (q_e) and the second order constants k_2 (g/mg. h) can be determined experimentally from the slope and intercept of plot t/q_t versus t.

RESULTS AND DISCUSSION

SEM and BET analysis

Fig. 1 depicts the SEM image (magnification = 1000×) of CAC-F200. It can be observed that the surface of CAC contains well developed pores in which there is a good possibility for carbofuran to be adsorbed. The BET surface area was 620.3 m^2/g.

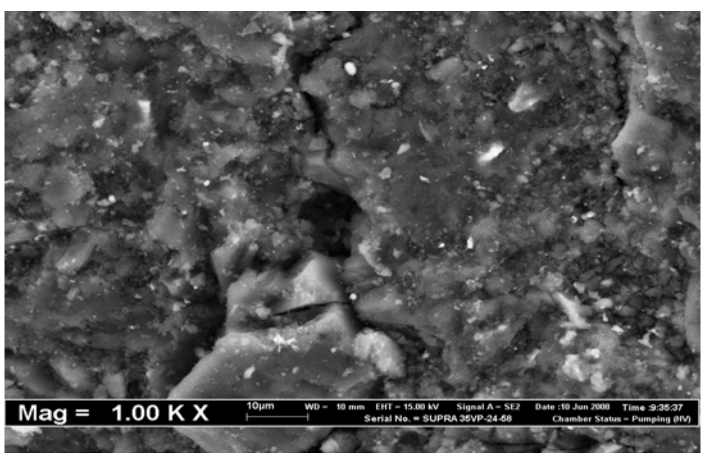

Fig.1: SEM micrograph for CAC-F200

Effect of initial concentration on the carbofuran adsorption capacity

The adsorption of carbofuran onto CAC-F200 was studied at different initial concentrations (50, 100, 150, 200 and 250 mg/L) respectivly. It can be seen from Fig. 2 that the amount of the adsorbed carbofuran at low initial concentration (50 mg/L) achieve adsorption equilibrium in aproximately 6 hours, while at initial carbofuran concentration of (100-150 mg/L) achieve adsorption equilibrium in aproximately 15 to 20 hours, the time necessary to reaches equilibrium for initial carbofuran concentration (200-250 mg/L) was more than 24 h.

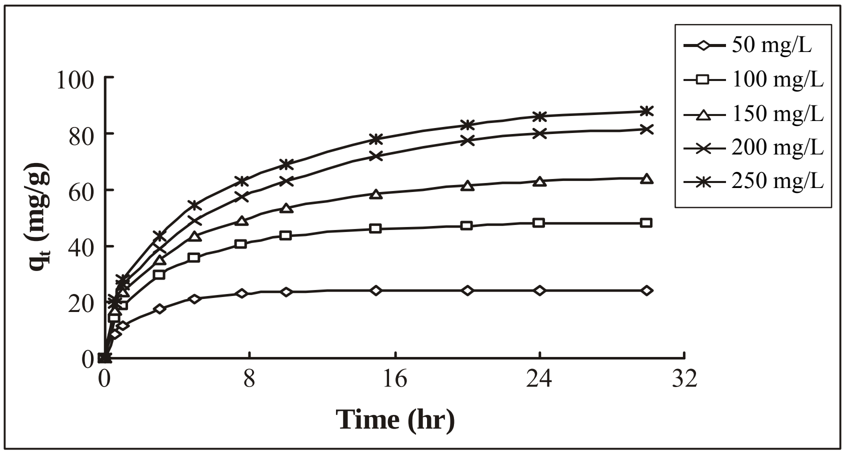

Fig. 2: Effect of contact time on the adsorption capacity for different carbofuran concentrations

Effect of solution pH on pesticide adsorption

The effect of pH on carbofuran adsorption was studied by varying the pH from 2 to 12 using 100 mg/L of fixed initial concentration of carbofuran at 30^{o}C. The variation of pH on equilibrium adsorption of carbofuran by CAC-F200 is as shown in Fig. 3.

The equilibrium adsorption capacity of carbofuran was found to decrease from 37 to 22.05 mg/g when the initial pH of the aqueous solution was increased from 2 to 12. This may be due to the presence of excess H^+ ions which accelerates the removal of the carbofuran with the anion OH^- in the aqueous solution. This means that adsorption of this pesticide is enhanced in the acidic medium. In acidic medium protonation occurs to the amino groups and the pesticide become positively charged. It was found in some unpublished experiments conducted to see the effect of acids and bases on this adsorbent that it reacts with both of them but with acids the reaction was more vigorous[10].

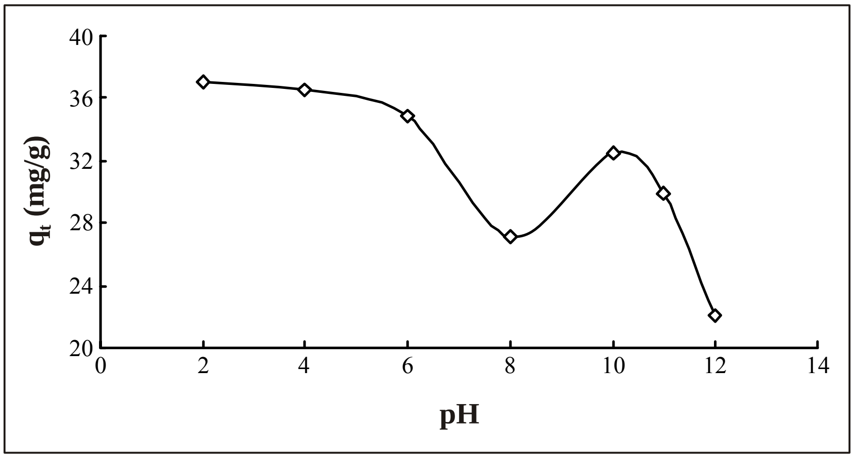

Fig. 3: Effect of pH on the adsorption rate of carbofuran onto CAC-F200

Equilibrium modeling

Adsorption isotherm was carried out using three isotherm models: the Langmuir, Freundlich and Temkin isotherm models. The linear plot of specific adsorption (C_e/q_e) against the equilibrium concentration (C_e) for Langmuir model, ($ln\ q_e$) against the *(ln Ce)* for Freundlich model and *(ln C_e)* against the equilibrium adsorption (q_e) for Temkin model (Figures not shown), it appeared that the adsorption obeys the Langmuir model having the highest value of correlation coefficient R^2. Table 1 summarizes the monolayer adsorption capacities according to the Langmuir model and the constants of the three isotherms together with their correlation coefficients at 30^{o}C.

Table 1: Langmiur, Frendulich and Temkin isotherm parameters

Isotherms	Parameters		
Langmuir	q_m (mg/g)	k_a (L/mg)	R^2
	97.1	0.126	0.99
Freundlich	K_F (mg/g(L/mg)$^{1/n}$)	n	R^2
	19.8	2.61	0.94
Temkin	A (L/g)	B	R^2
	1.59	19.33	098

It was observed that the Langmuir model yielded the best fit at all temperatures since the R^2 values were equal to 0.99 confirmed that the Langmuir isotherm was favorable for adsorption of carbofuran on CAC-F200 at 30°C.

Adsorption kinetics

The linear plot of t/q_t versus t (Figures not shown) for the pseudo second order model yielded R^2 values equal to values ≥ 0.999, for all carbofuran concentrations and this showed a good agreement between the experimental and the calculated q_e values the calculated q_e as mention in Table 2. In the mean time the linear plots were made for pseudo first order model (Figure not shown) which showed values deviated between the experimental q_e and the calculated q_e values.

Table 2: Pseudo second order kinetic model parameters

Initial conc. (mg/L)	Pseudo second order kinetic model			
	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	k_2 (g/mg.h)	R^2
50	24.25	25.5	0.040	0.999
100	47.76	49.11	0.012	0.999
150	63.25	65.03	0.006	0.996
200	79.88	80.21	0.004	0.993
250	85.85	86.3	0.003	0.991

CONCLUSION

The present investigation showed CAC- F200 to be a promising adsorbent for the removal of carbofuran from aqueous solutions over a wide range of concentrations. Equilibrium data were fitted to Langmuir, Freundlich and Temkin isotherms. The equilibrium data were best described by the Langmuir isotherm model, with maximum monolayer adsorption capacity of 97.1 mg/g for carbofuran, respectively. Thus the CAC–F200 has shown to be quite efficient in removal of pesticides from aqueous solution.

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