Studies of the Adsorption Thermodynamics of Carbofuran on Fly ash.

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Abstract:

The adsorption thermodynamics of carbofuran on fly ash at 25°C and 50°C have been studied via the relevant adsorption isotherms, Freundlich constants (K, and N), distribution coefficient (Kd) and other thermodynamic parameters. The data were well fitted by the Freundlich equation and yielded S-shaped isotherms at both the temperatures studied. Thermodynamic parameters such as the thermodynamic equilibrium constant (Ko), the standard free energy change (ΔG°), the standard enthalpy change (Δ H°) and the standard entropy change (Δ S°) have been calculated as a means of predicting the nature of the adsorption process.

Keywords: Adsorption, thermodynamics, Carbofuran, Freundlich Equation, Fly ash.

Introduction

fly ash, an industrial waste product, are produced in India by coal-based power steel plants. It has been reported that fly ash has an adsorptive potential which may help in removal of organic acids (Ahmed et al. 1983) and other toxic ions from water(Nadar and Parvath 1982, Prabhu et al. 1981). Eiceman and Vandiver (1983) reported that polycylic aromatic hydrocarbons are adsorbed on fly ash and it has also been used effectively for the soil acidity (Adriano 1980; Elseewi et al. 1980; Lal et al. 1996a) as well increasing the availability of certain plant nutrients in soil (Jones and Straughan 1978., Elseewi et al. 1981 ; Druzina et al 1983 ., Maiti et al. 1990; Sikka and Kansal 1994; Lal et al. 1996b; Oswal et al .1997) The treatment of soils with fly ash has led to a reduction in the population of plant parasitic nematodes (Haq et al .,1985). Carbofuran(2,3-dihydro-2,2-dimethyl-7- benzofuranyl methyl carbamate) a systemic, non-ionic broad spectrum carbamate insecticide / nematicide which has been widely used in Indian agriculture on a large scale for the control of nematodes in soils. Its structure can be represented as follows:

The excessive use of carbofuran becomes a source of pollution in soil and sub-soil water. Considerable work has been done on the factors affecting the adsorption of pesticides in soils (Bailey and White , 1970). Singh et al ,1985) have studied the adsorption thermodynamics of carbofuran only on soils, but nothing is known about its adsorption on fly ash in case both are applied to soil to reduce the nematode population. Therefore, an attempt was made to study the adsorption thermodynamics of carbofuran on fly ash in order to understand the role of fly ash in the removal of pollutants.

Experimental.

Materials and Methods

The fresh sample of fly ash (200-300 mesh size) used in this study was obtained from Kota Thermal Power Plant, Rawatbhata , Rajasthan, India and possessed the following charastricts : sand , 65.5% ., silt ,32.8%, clay, 1.7% ; pH (1:2), 6.07 ;EC (ds/m 0.81 ., CEC , 24 (cmol /kg) ., bulkdensity 1.18 Mg /M ., organic carbon , 0.114 % .,   WHC, 64.5 % ., surface area, 650 m2 /g. All these various parameters were determined by the use of standard techniques.

 A shaking incubator with a temperature variation of ±1°C was used for all adsorption studies, and a Bausch and Lomb Spectronic-20 spectrophotometer was used for carbofuran determination.The surface area of fly ash determined by the ethylene glycol method was found to be 680 mg¹.

The adsorption studies were carried out by placing 1 g fly ash sample in 20 ml of distilled water, containing varying concentrations of carbofuran. The tubes were shaken for 3 h at 25±1°C for the first set of experiments and at 50±1°C for the second set of experiments in a shaking incubator. The mixtures were centrifuged at 3500 rpm for 10 minutes and the carbofuran was estimated in the supernatant liquid spectrophotometrically (Mithynathan and Perur , 1974). The amount of carbofuran adsorbed was determined as the difference between the amount of carbofuran added and that left after adsorption. All the studies were repeated twice.
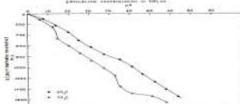

Fig. 1. Adsorption isotherms of carbofuran on fly ash at 25 and 50 °C

Results and Discussion

Adsorption isotherms of carbofuran on fly ash at 25°C and 50°C were constructed connecting the amount of carbofuran adsorbed (ug/g) and the amount of carbofuran remaining in suspension (ug/ml) at equilibrium (Figure 1). The isotherms depicted in the figure are similar to the S-shaped isotherms defined by Giles et al (1960) and suggest that the adsorption process was more effective at higher concentrations. The isotherms also indicate that adsorption decreased with increasing temperature. The decrease in the percentage of carbofuran adsorbed with increasing concentration may probably be attributed to saturation of the fly ash adsorption sites. Since carbofuran molecules are adsorbed on fly ash as a single monofunctional unit, there appears to be a marked localization of the attractive forces at the carbonyl of group which leads to very high interaction with the fly ash at this point in the molecule (Singh et al , 1985) The lower extent of carbofuran adsorption exhibited at 50°C is partly due to a weakening of the attractive forces between carbofuran and fly ash sites and partly to enhancement of the thermal energy of the adsorbate, thereby making the attractive forces between the adsorbate and adsorbent insufficient to retain the carbofuran molecule. However, the nature of the adsorption process remains unaffected under these conditions.

The stastical average of all Kd values was calculated by using linear regression equation forced through the origin:

$$K_d = \Sigma\left(\frac{x}{m}\cdot C_e\right)/\Sigma C_e^2$$

Where   stands for the summation of the measured values.The values of Kd recorded are 26.90 and 20.20 at both 25°C and 50°C. temperatures.The greater adsorption at 25°C was also confirmed when Kd values was taken in to consideration.

Greater adsorption at 25°C was also confirmed when Kd, values were taken into consideration.

This adsorption behaviour of carbofuran on fly ash at both temperatures was in close agreement with the Freundlich equation. The Freundlich constants K and N were obtained from the linear regression analysis of log x /m = log K+ N log Ce ---(2)

where x/m is the amount of carbofuran adsorbed per gram fly ash (ug / g) and Ce is the concentration (ug / ml) of carbofuran in equilibrium suspension. K and N are determined from the intercept and slope of the curve, respectively. The values of K and N were 32.65 and 0.9543 at 25°C; 10.08 and 1.1768 at 50°C . This again indicated higher adsorption of carbofuran at low temperatures. These results in a way conform with those of Singh et al., (1985) who worked on the adsorption of carbofuran by soils and with those of Van Bladel and Moreale (1970) regarding the adsorption of Fenuron and Monuron on montmorillonite.

The thermodynamic equilibrium constant Ko , for the adsorption reaction was calculated by the method of Biggar and Cheung (1973) as applied by Singh et al. (1985) and Varshney et al. (Varshney el al ., 1986).

$$K_0 = \frac{C_s}{C_e}\cdot\frac{v_s}{v_e} \qquad (3)$$

where Ce (ug / g) is the amount of carbofuran adsorbed per gram of the solvent in contact with fly ash, Ce (ug / ml) is the concentration of carbofuran in equilibrium suspension, V, is the activity coefficient of the adsorbed solute and Vs , is the activity coefficient of the solute in equilibrium suspension. The ratio of activity coefficients was assumed to be unity (Robension and Stokes (1959) in the dilute range of the studies.

The value of Cs , was calculated using the equation proposed by Fu et al. (1948).

$$K_d = \Sigma\left(\frac{x}{m}\cdot C_e\right)/\Sigma C_e^2 \qquad (4)$$

where p is the density of the solvent (g /ml), M the molecular weight of the solvent, A the cross-sectional area (cm² molecule¹) of the solvent molecule, N is Avogadro's number, S the surface area of the adsorbent (m²/ g) and x/m the specific adsorption (mmol / g). The cross-sectional area (A) of the solvent molecules was estimated by using the following equation (Kodera and Onishi 1959).

$$A = 1.091\cdot 10^{-16}\left[\frac{10^{24}M}{N}\right]^{2/3} \qquad (5)$$

As the concentration of solute in the solution approached zero, the activity coefficient, V ,approached unity. Equation (4) may then be written as

$$\lim_{C_\varepsilon \to 0} \frac{C_s}{C_\varepsilon} = K_o \qquad (6)$$

The values of Ko , were obtained by plotting In (Cs/Ce) versus Cs and extrapolating to zero Cs=0. The value of Ko , $5.46 \times 10 \times 9$ was higher at 25°C than at 50°C ($7.40 \times 10 \times 8$ which again confirmed that fly ash had a higher affinity for carbofuran at low temperature.

The standard free energy changes ($\Delta G°$) for the interaction of fly ash with carbofuran were calculated from the relationship (Glasstone 1960).

$\Delta G° = RT$ In Ko-----(7)

The standard enthalpy change (AH) was calculated from the Van't Hoff isochore

$$\ln \left(\frac{K_{T_2}}{K_{T_1}} \right) = \frac{-\Delta H^0}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right] \qquad (8)$$

and the standard entropy change, $\Delta S°$, from the equation

$\Delta G° = \Delta H° - T\Delta S°$----(9)

The results thus obtained are given as follows : at 25 ℃ , $\Delta G°$(kJ / mol) -55.32, $\Delta S°$(kJ/k / mol) -0.028) and at 50°C , $\Delta G°$ (kJ / mol) -54.61 $\Delta S°$ (kJ /K /mol) -0.280) .The $\Delta S°$ for both the temperatures is - 63 .72 .

These results show negative values of $\Delta G°$ at both tem- peratures. Thus it supported the above view that fly ash had a higher affinity for carbofuran, which might be due to weak attractive forces at the higher temperature. This also confirms the nature of the isotherms obtained at the two temperatures (Fig. 1). The enthalpy effect indicated that the reaction was temperature-dependent and exothermic. It also indicated that cabofuran was more strongly bound to fly ash with energetically stable products having high degree of binding for carbofuran with fly ash sites. A negative entropy change ($\Delta S°$) indicated a greater order of reaction during adsorption of carbofuran on fly ash at both temperatures.

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