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LINDANE ADSORPTION-DESORPTION ON CHITIN IN SEAWATER

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The adsorption and desorption processes by solid materials are important in determining the movement and fate of pesticide compounds in aquatic systems. Chitin is one of the constituents of natural organic matter and may serve as a model organic phase for studying the pesticide adsorption-desorption in marine systems. The lindane adsorption-desorption to chitin has been studied as a function of chitin concentration ($2.5\ \mathrm{g l^{-1}}$ to $12.5\ \mathrm{g l^{-1}}$), temperature (5 to 45°C), pH (1.5 to 8) and salinity (15‰ to 36‰). Both, Freundlich and linear isotherms for the adsorption and desorption processes were used to represent the experimental data. Two-site Langmuir isotherm can describe well the measured sorption isotherm. The adsorbent-concentration effect and the adsorption-desorption hysteresis show the existence of different classes of site with different accessibility. Thus, the adsorption-desorption reaction of lindane is the result of more than a single mechanism. An increase in temperature ($\Delta H = -4.0 \pm 0.7\ \mathrm{Kcal\ mol^{-1}}$) and a decrease in salinity resulted in both lower lindane adsorption and in a more reversible process. An increase of pH resulted in lower adsorption partition coefficients.

KEY WORDS: Adsorption, desorption, lindane, chitin, seawater.

INTRODUCTION

The ubiquitous contamination of natural ecosystems with chlorinated pesticides has been well documented[1]. These compounds are transported from areas of application and disposal to the marine environment via the atmosphere, rivers and land drainage, as well as direct introduction via domestic and industrial waste.

The exchange of pesticides between dissolved and sorbed states is a primary mechanism involved in the transport and fate of these compounds in ground and surface waters. As a result of sorption the concentration in the liquid phase is lowered and since the water and the solid usually have different velocities, binding of the compound to the surface could provide a means for transporting these persistent pollutants through the water column and for concentrating them in sediments and in benthic and planktonic detritus-feeding organisms.

The sorption of pesticides by solid materials has been reported by a number of investigators[2–6]. These studies support the hypothesis that suspended materials are likely to be a major transport medium for certain substances, as determined by the extent to which such substances partition to solid materials. Pierce *et al.*[7] suggested that chlorinated hydrocarbons could have a greater affinity for hydrophobic sites on organic particulates than for a hydrophilic adsorbent like clay. Available mathematical models of the behaviour of pesticide in solid materials usually assume that the pesticide in the liquid phase is in equilibrium with that adsorbed by the solid phase and that this equilibrium is correctly assessed via adsorption experiments[8]. This simple partitioning model implies that sorption is reversible and can be described well by a linear relationship, i.e., a linear Freundlich isotherm.

Chitin (poly-*N*-acetyl D-glucosamine) is probably one of the most abundant natural marine polysaccharides, forming the exoskeleton of most of the invertebrates[9]. Chitin is consequently abundant in natural environments.

The sorption properties of chitin were first studied by Hackman[10] in relation to the sorption of proteins in aqueous solutions. In the past several years, chitin has been used as a sorbent for thin layer and high pressure liquid chromatography[11–13] and as a chelating polymer for bonding toxic metal ions in natural waters[14–16] and in seawater[17,18].

In spite of the natural abundance of chitin, very little research has been conducted on the interaction of pesticide with the polymer. Richards and Cutkomp[19] and Lord[20] showed that chitin binds DDT.Daver and Whightman[21] studied the uptake isotherms of 2,4-D, dicamba, 2,4,5-T, MH and MCPA on chitin and chitosan, its deacetylated derivative. McCormick and Anderson[22] studied chitin which had herbicides chemically attached to increase pesticide efficiency and reduce the mobility of the active agents in the environment.

The aim of this work was to determine if chitin can serve as a model organic phase for the study of pesticide adsorption-desorption in marine systems. We examine the lindane adsorption-desorption rate on chitin, its adsorption-desorption isotherms, taking into account the effect of the concentration of adsorbing solids on the partition coefficients and developing functional forms to define the relationship. The measurements were made also as a function of pH, salinity and temperature in an attempt to better understand the mechanism of the adsorption-desorption process.

EXPERIMENTAL

The chitin powder used (Sigma Chemical Co., MO, U.S.A.) was derived from crab shells. Previous studies using water-prewashed chitin to eliminate macromolecules and nonsettling particles do not show noteworthy effects. In all the experiments, chitin was used without further purification. The surface measured by the BET method using krypton as the adsorbate was $0.5 \pm 0.03\ \mathrm{m^2\,g^{-1}}$ for the bulk chitin used in most of the experiments[17]. Preliminary studies with different fractions ranging between 250 μm to lower than 88 μm gave similar adsorption results to the bulk, which was used in all the following studies. Seawater ($S = 36.52$) from Gran Canaria (The Canary Islands) was 0.45 μm filtered and hexane-preextracted prior studies to eliminate the particulate matter and any dissolved organics. Stock solutions containing $75\ \mathrm{mg\,l^{-1}}$ lindane (99% purity) (Supelco Inc., Bellefonte, PA, U.S.A.) were prepared in pesticide grade hexane.

All batch sorption studies (in triplicate) involving the equilibration at the desired controlled temperature bath were carried out in glass-stoppered centrifuge glass tubes (volume: 50 cm^3). The lindane solution (ranging from 1 $\mu g\,l^{-1}$ to 685 $\mu g\,l^{-1}$) was added, and after hexane evaporation, 40 ml of seawater was added. After a 24 h preequilibration period, the mass of chitin was added (from 2.5 $g\,l^{-1}$ to 12.5 $g\,l^{-1}$). The solution pH values were adjusted by adding 0.01 M HCl or NaOH. The seawater pH measurements were calibrated using Tris-seawater buffers and made on the free proton scale[23]. The glass tubes were shaken in the controlled temperature bath for 24 h when equilibrium conditions were desired. For adsorption rate experiments, the time of shaking was varied accordingly. After shaking, the supernatant was centrifuged for 15 min at 6,000 rpm. A 25 ml aliquot of the centrifuged solution was extracted in 10 ml pesticide grade hexane during 60 min in an orbital shaker at 160 rpm. In the recovery studies, repeated extractions showed the first extraction removed over 97% of the lindane mass. Extracted samples were analyzed and quantified by gas chromatography. Analyses were carried out on a Perkin Elmer 8500 gas chromatograph equipped with a Ni^{63} ECD. A SPB-5 (Supelco, Inc.) 30 m-fused silica capillary column was used with N_2 carrier gas at a linear velocity of 25 cm s^{-1}. Samples were analysed isothermally (200°C) in on-column injection and at a detector temperature of 300°C.

The pesticide mass in the test sorption system was derived from triplicate measurements by comparing their peak area responses occurring at the appropriate retention time with a standard curve prepared from standard solutions of the pesticide at the same experimental conditions. Coefficients of variation of these triplicate measurements were about 1%. It was assumed that the difference between the pesticide mass added and the pesticide mass in the liquid phase at the end was the result of chitin sorption.

The desorption tests were similar to the adsorption tests, except that after the equilibration and phase separation the supernatant was replaced with contaminate-free seawater and the glass tubes were placed back into the shaker and allowed to equilibrate for 24 h. The desorption kinetics were measured after 24 h adsorption equilibration for periods between 5 min to 72 h.

RESULTS AND DISCUSSION

Adsorption-desorption kinetics of lindane An assessment of lindane chitin-seawater interaction in natural systems requires an evaluation of the rate at which the partitioning process occurs. Previous works on a variety of organic compounds[2,24,25] suggest that the partitioning process for physical adsorption to sediments occurs quite rapidly (hours). Partitioning of lindane (187.5 $\mu g\,l^{-1}$) to 6.25 $g\,l^{-1}$ chitin concentration as a function of the equilibration time, for periods ranging from 2 min to 72 h shows the process occurs quite rapidly. In about 3 h, the adsorption process is essentially complete and it may be followed by a much slower penetration or diffusion of the pesticide molecule into the structure of the surface of the chitin, which is similar to other studies on organic partitioning between the sediment and water phases[24,26,27]. This would seem to be the result of a weak physical adsorption of organic molecules at sediment particle surfaces[28]. Although 3 h adsorption time would appear to be sufficient, a 24 h equilibration period was chosen for all adsorption experiments.

For the study of the effect of the desorption time on the desorption partition coefficient, vessels were equilibrated for $t_a = 24$ h followed by the desorption step. Because of the importance of this observation to the interpretation of the extent of reversibility of lindane adsorption, long periods of desorption (up to 72 h) were employed. However, the results indicate that the desorption is essentially complete in a few minutes and much longer desorption times do not produce notable effects on the amount desorbed. In all the studies, a 24 h equlibration period was chosen for desorption experiments.

Adsorption-Desorption Isotherms The results of measurements on adsorption equilibria can be used to determine the affinity of chitin for lindane by calculating the corresponding partition coefficients. It is usual for the results of pesticide-sorption experiments to be expressed adequately by the Freundlich isotherm equation[6,29–31] due to the fact that this isotherm has been empirically associated with specific types of adsorption.

$$C_s = K_F C_w^{1/n} \tag{1}$$

where C_s, is the mass of pesticide sorbed divided by the mass of the solid phase (kg kg^{-1}), C_w is the mass concentration of pesticide in the liquid phase (kg m^{-3}), and K_F and $1/n$ are the Freundlich isotherm parameters. When the studies are made at dilute pesticide concentrations a linear isotherm can be fitted[27,32] which represents a special case of the Freundlich equation ($n = 1$)

$$C_s = KC_w \tag{2}$$

The results of the lindane adsorption measurements on chitin in seawater are shown in Figure 1. Only the average of the triplicate samples are shown, because the individual points almost coincided (measured concentrations in the liquid phase in triplicate samples always differed from each other in less than 5%). It shows first, that the adsorption isotherms of lindane can be described well with the Freundlich sorption isotherm Eq. (1) (Table 1), and second, a general trend towards a decreasing partition coefficient with the increasing concentration of chitin, as has been indicated for other pesticide-solid adsorption processes[27,30–34] (Table 1). When the initial lindane concentrations are below 450 μg l^{-1}, linear isotherms can be fitted (Eq. (2)). The linear partition coefficients and correlation coefficients are shown in Table 1.

In pesticide/soil systems, the properties of sorption sites can be expected to be heterogeneous and various sorption mechanisms can operate. Chitin surface contains various functional groups[17] and may present a very heterogeneous surface to lindane molecules ranging from easily accessible surface sites to less accessible internal voids. Next we attempted to describe the measurements with the sum of two-site Langmuir isotherm covering adsorption at two types of site with different properties at the molecular level. This yields[29]

$$C_s = C_{s,1} + C_{s,2} = \frac{b_1 K_{L,1} C_w}{1 + K_{L,1} C_w} + \frac{b_2 K_{L,2} C_w}{1 + K_{L,2} C_w} \tag{3}$$

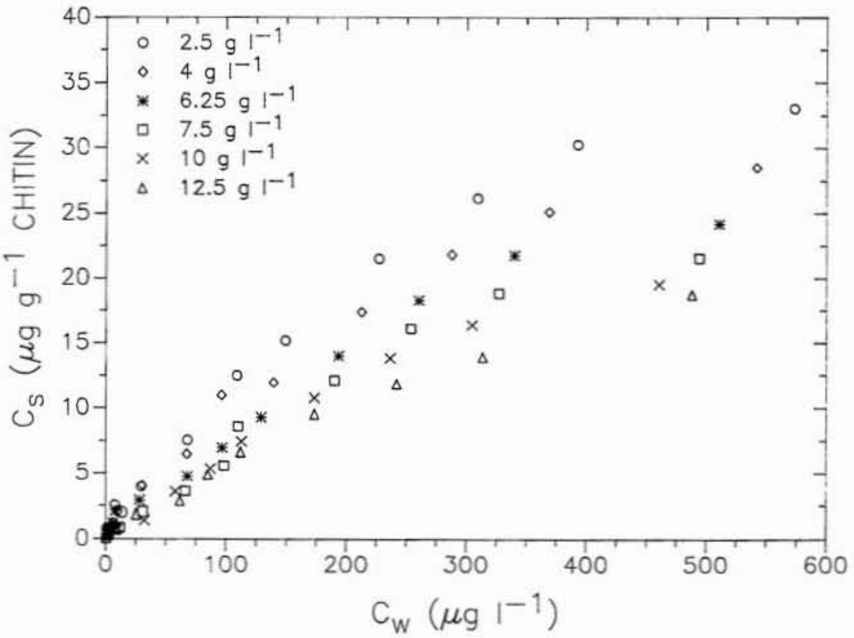

Figure 1 Adsorption isotherm of lindane and chitin in natural seawater as a function of the chitin concentration. Data are plotted according to the Freundlich Equation (1). The difference between the pesticide mass added and the pesticide mass in the liquid phase is assumed to be the result of chitin adsorption.

in which the subscripts 1 and 2 refer to two different sites and b_1 and b_2 are the maximum content sorbed (kg kg^{-1}) on sites 1 and 2, respectively. Sites 1 and 2 are assumed to be different at the molecular level, resulting in different values for K_L.

Measured sorption isotherms were fitted to Eq. (3) using the interpolation method described by Sposito[35]. The optimized values of the parameters of Eq. (3) are shown in Table 2. We conclude that measured sorption isotherms could be described well

Table 1 Values of parameters in the equations for the Freundlich and linear isotherms (Eqs. (1) and (2)), as derived from measured sorption isotherms of lindane

[Chitin] g l^{-1}	*Freundlich isotherm*			*Linear isotherm**	
	$K_F(l^{1/n}/g^{1/n})$	*$1/n$*	*r*	*$K_a(l\,g^{-1})$*	*r*
2.5	0.35 ± 0.06	0.75 ± 0.04	0.992	0.080 ± 0.004	0.989
4	0.26 ± 0.06	0.78 ± 0.05	0.986	0.067 ± 0.004	0.989
6.25	0.18 ± 0.05	0.81 ± 0.05	0.999	0.062 ± 0.003	0.992
7.5	0.14 ± 0.03	0.82 ± 0.05	0.995	0.060 ± 0.002	0.994
10	0.10 ± 0.02	0.88 ± 0.04	0.989	0.055 ± 0.002	0.996
12.5	0.09 ± 0.03	0.87 ± 0.06	0.976	0.048 ± 0.002	0.992
2,000†	0.35	0.944			

* Values corresponding to initial concentrations lower than 450 μg l^{-1} of lindane.

† Lindane adsorption on aquifer sands[6].

Table 2 Values of parameters in the equation for the sum of two Langmuir sorption isotherms (Eq. 3), using an interpolation method[35], as derived from the measured sorption isotherms of lindane (standard deviations are in parentheses)

[Chitin] g l^{-1}	$b_1 (\mu g\ g^{-1})$	$b_2 (\mu g\ g^{-1})$	$K_{L,1}/10^3\ (l\ g^{-1})$	$K_{L,2}/10^3\ (l\ g^{-1})$
4	2.07 (0.31)	58 (8)	390 (148)	1.8 (0.3)
6.25	1.21 (0.22)	52 (8)	627 (185)	1.7 (0.4)
10	0.94 (0.14)	44 (4)	674 (173)	1.8 (0.2)
1000*¹	0.010 (0.002)	10 (1)	40 (10)	0.07 (0.01)
1000*²	0.007 (0.003)	4.1 (0.5)	30 (10)	0.08 (0.01)

* Values for cyanazine (1) and metribuzin (2) pesticides adsorbed to a calcereous loamy sand[29].

by Eq. (3). However, this is not conclusive for the existence of only two types of sorption sites in chitin. Whilst the $K_{L,2}$ values are quite constant, the values of $K_{L,1}$, b_1 and b_2 are affected by the chitin concentrations. As a first approximation, the sorption sites on chitin can be divided into two classes: sites of the one class are located on the external surface, those of a second are located within the porous aggregate on the internal voids[3]. It must be stressed that the distinction between the two classes of site is based purely on differences in accessibility; at the molecular level, the properties of sites (type 1 and type 2 sites) within each class can be expected to be heterogeneous.

Additional information about the mechanism of adsorption was obtained by studying the desorption process of lindane released from contaminated chitin. The sorptive reaction has been reported to be both reversible and nonreversible[27,31,36]. Whilst the theoretical models all assume a condition of dynamic equilibrium and complete reversibility, this assumption is dubious in the case of hydrophobic compounds. The partition coefficients for the linear desorption isotherms for most of the chitin concentrations studied exhibited significant nonreversibility (Figure 2). Adsorption partition coefficients were consistently lower (K_a from 80 to 45 l kg^{-1}) than the desorption partition coefficients (K_d values from 430 to 60 l kg^{-1}) (Figure 3) (Table 3). A useful index of reversibility is the ratio of desorption to adsorption partition coefficient K_d/K_a which approximates unity for complete reversibility and increases as nonreversibility increases. As can be seen in Figure 3 and Table 3, the sorption process comes close to complete reversibility when high chitin concentrations (more than 10 g l^{-1}) are present. The behaviour of both the adsorption K_a and desorption K_d partition coefficients as a function of chitin concentration is somewhat more complicated. They are nearly equal at high adsorbent concentrations ($m = 12.5$ g l^{-1}) and both decrease as m increases. However, the desorption partition coefficient varies more markedly than the adsorption partition coefficient (Figure 3).

Effect of temperature Although the range of temperature variations generally found in seawater varies slightly with seasonal changes, the seawater column temperatures typically range from minus 5°C to 30°C during a yearly cycle. Experiments were conducted in the hope that they might further the understanding of the sorption process. Adsorption-desorption isotherms were made at 5 ± 0.1°C, 20 ± 0.1°C and

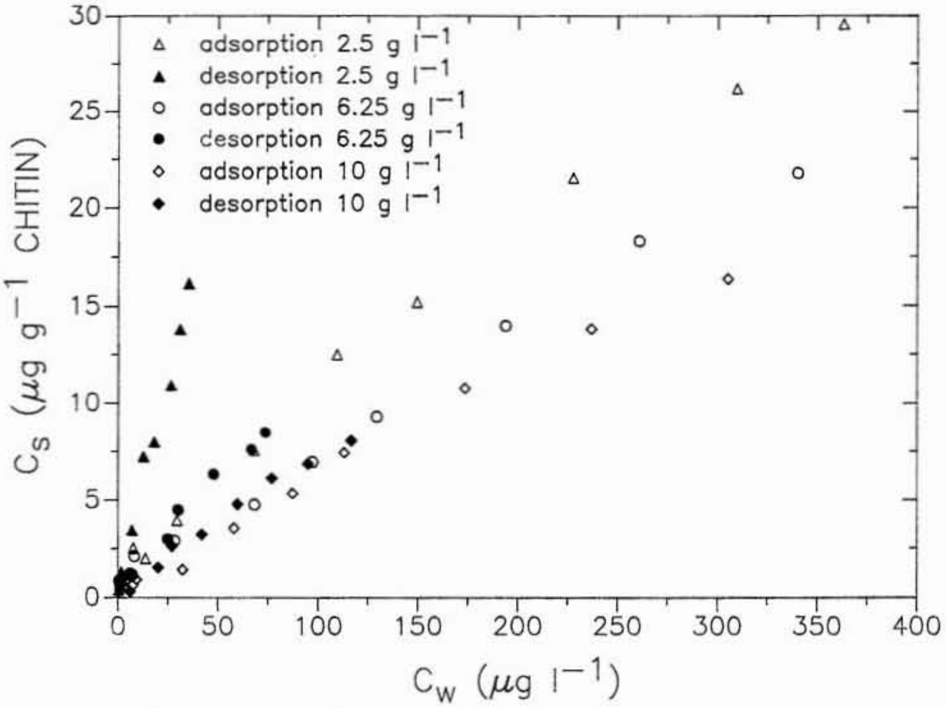

Figure 2 Lindane adsorption-desorption isotherms for three chitin concentrations. At low chitin concentrations a nonreversible behaviour is observed. Time of adsorption and desorption, 24 h.

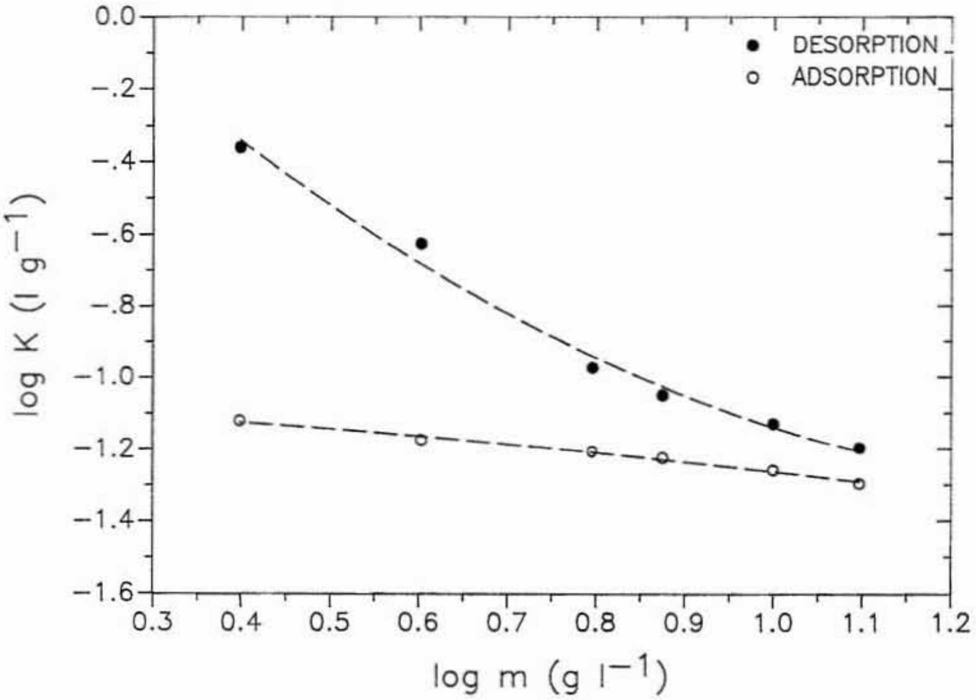

Figure 3 Effect of chitin concentration on the adsorption and desorption partition coefficient of lindane in seawater as determined using a linear isotherm.

Table 3 Isotherm parameters*, their coefficient of variation, and the nonreversibility index for lindane adsorption-desorption to chitin in seawater

[Chitin] g l^{-1}	*Adsorption K_a ($l\ g^{-1}$)*	*Desorption K_d ($l\ g^{-1}$)*	*Nonreversibility index K_d/k_a*
2.5	0.0801 ± 0.0039	0.430 ± 0.018	5.4694 ± 0.04
4	0.0673 ± 0.0038	0.234 ± 0.028	3.5369 ± 0.21
6.25	0.0621 ± 0.0027	0.106 ± 0.004	1.7094 ± 0.01
7.5	0.0596 ± 0.0019	0.089 ± 0.006	1.4945 ± 0.06
10	0.0551 ± 0.0017	0.074 ± 0.004	1.3435 ± 0.03
12.5	0.0480 ± 0.0018	0.060 ± 0.002	1.3785 ± 0.01
20†	0.04 ± 0.26	0.05 ± 0.15	2.33 ± 0.30

* Values corresponding to initial concentrations lower than 450 μg l^{-1} of lindane.
† Hexachlorobiphenyl adsorption-desorption on Lake Huron (Michigan) sediments[27].

45 ± 0.1°C, and the corresponding K_a and K_d partition coefficients plotted in Figure 4. Both adsorption and desorption partition coefficients show significantly reduced adsorption on chitin at higher temperatures.

By analogy to the Clausius-Clapeyron equation, the apparent heat of adsorption of lindane on chitin has been estimated from the expression[37]

$$\frac{\delta \ln p}{\delta 1/T} = -\frac{\Delta H}{R} \tag{4}$$

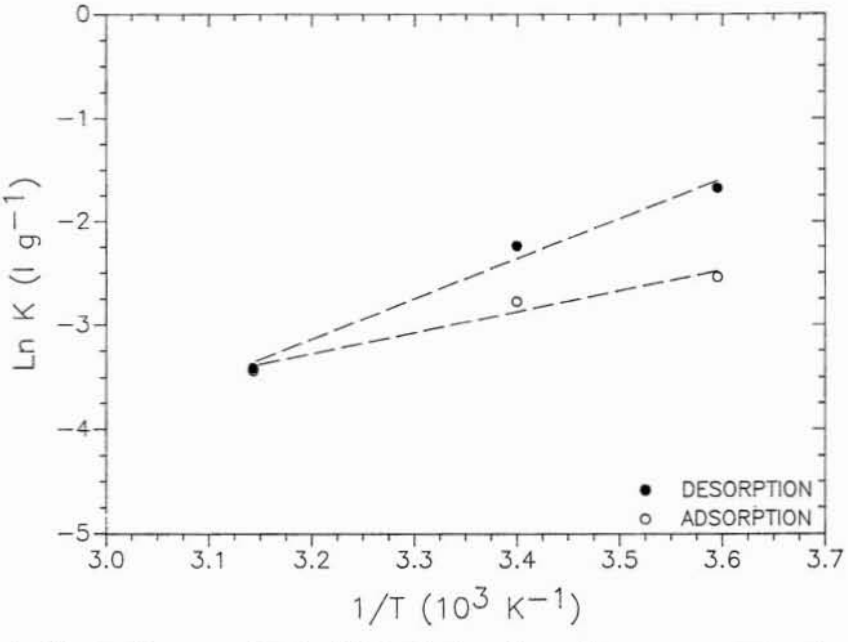

Figure 4 Clausius-Clapeyron plot (Eq. (4)) for the dependence of temperature on the adsorption and desorption partition coefficients. Chitin concentration, 6.25 g l^{-1}.

A negative value of $\Delta H = -4.0 \pm 0.7$ Kcal mol^{-1} is found[3,6,8] for the adsorption in accordance with the predicted value for an exothermic adsorption process. The magnitude of the apparent heat of adsorption falls within the range usually expected for physical adsorption to sediments[28]. The relatively non-reversible lindane bonding implied by the partitioning studies appears to clash somewhat with calculations of the enthalpy of adsorption based on variations in adsorption and desorption with temperature and it must be viewed with caution since the Clausius-Clapeyron equation becomes invalid. However, it is observed that at a high temperature, the adsorption-desorption process becomes reversible due to both a weakening of the attractive forces between the solute and the chitin surface and reaction rates for the desorption process may increase with increasing temperature[27]. Any increase in solubility of the lindane in the solvent has been compensated by preparing different blanks at the same experimental conditions.

Effect of pH Figure 5 depicts the results of experiments conducted to assess the effect of the pH on lindane partitioning to 6.25 g l^{-1} chitin concentration in seawater. To compensate the lindane decomposition due to the pH effect, blanks for each pH value were prepared using the same experimental conditions. The results indicate a significant reduction in lindane adsorption by the chitin as the pH level was increased over a range from pH = 1.5 to seawater pH (8.2). The data suggest a rather abrupt decrease in K_a as the solution pH level increases from pH = 2.5 to pH = 5. Values of K_a for very acidic solutions (pH < 2.5) are approximately 2–3 times greater

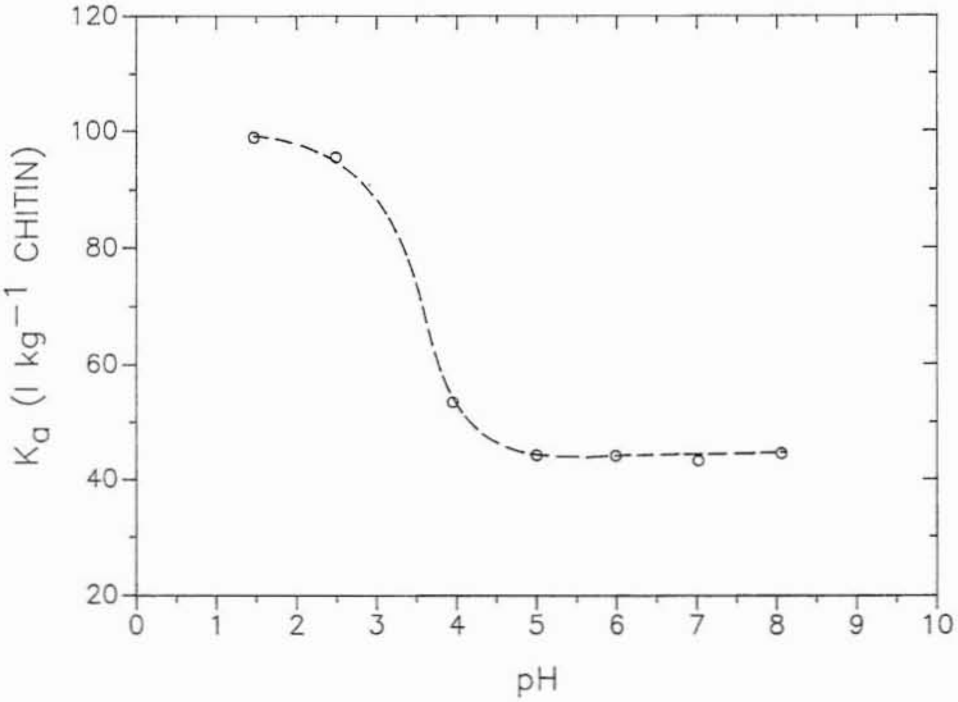

Figure 5 Effect of pH on the lindane adsorption partition coefficient to 6.25 g l^{-1} chitin concentration. The pH of the seawater is adjusted by addition of NaOH and HCl.

between Log K_a and Log K_d vs $S^{1/2}$ gives a positive slope of 0.048 ± 0.011 and 0.1436 ± 0.0054 respectively, results which are in concordance with those obtained by Karickhoff *et al.*[36] for the adsorption of pyrene in water. The data suggest a significant decrease in the nonreversible behaviour of the adsorption-desorption process as salinity decreases. This may result in chitin being an important agent in accumulating and transporting lindane from natural water, in estuaries and lakes, to seawater, where the quantity of chemical desorbed is much less than the quantity of chemical adsorbed.

From the results of the different studies, the lindane adsorption-desorption distribution was used to gain insight into the adsorption mechanism. The adsorption of organochlorine pesticides to organic particulates has been attributed to hydrophobic bonding to portions of natural organic polymers[7]. Khan and Schnitzer[38] suggested that hydrogen bonding between organic polymers could form internal voids which trap hydrophobic molecules. The adsorbing capacity of chitin observed in the present study may be due to a chitin-lindane interaction of a hydrophobic nature, together to coulombic attraction because of the salinity effect on the adsorption and desorption processes. Nonpolar portions of the chitin polymer and lipoidal molecules trapped within the polymer could provide hydrophobic bonding sites for lindane[3]. It is also possible that lindane molecules could become trapped within voids in the polymer.

The nonreversibility shown by the chitin partition curves (Figure 2) reveals that the equilibrium was not the same in effect for desorption as for adsorption conditions. It appears that the observed adsorption of lindane is the result of more than a single mechanism. We may postulate that due to the heterogeneous chitin surface to lindane molecules, the compliance of the two-site Langmuir isotherm and the shift in equilibrium for the desorption resulted from heterogeneous, hydrophobic bonding sites of differing strength throughout the chitin polymer.

CONCLUSION

It has been demonstrated that lindane can be absorbed by chitin surfaces in seawater. The adsorption of lindane on chitin can be correlated with a Freundlich isotherm, but at low lindane concentrations a single adsorption isotherm can be used properly. The two-site Langmuir isotherm covering adsorption at two types of sites suggests the existence at least of two classes of sites, which participate in the adsorption and could explain the effect of solid concentrations on the partition coefficients. Only at high chitin concentrations does the adsorption-desorption process become completely reversible. At lower chitin concentrations, the lindane adsorbed on the internal surface and on the strongest bonding sites may cause the nonreversibility observed. The decrease in the adsorption partition coefficients as solution pH levels increase may be related to changes in the charge characteristics of chitin surfaces. Variations in factors such as temperature and salinity have additional (positive and negative) effects on the availability of lindane and show that the adsorption-desorption process becomes reversible at high temperatures and low salinities.

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