

The Adsorption of Cd(II) and Pb(II) to Chitin in Seawater

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The adsorption of Cd²⁺ and Pb²⁺ to the surface of chitin has been studied in seawater as a function of pH (2 to 8), temperature (5 to 60°C), salinity (4 to 36), and the presence of other transition metals. The rates of adsorption were quite rapid ($t_{1/2} = 20$ min) and were affected by the presence of other metals such as Cu²⁺. For Pb²⁺, a Langmuir-type adsorption equilibrium was used to represent the experimental data. The Langmuir stability constant, K_L , was 1.9×10^{-10} mg mol⁻¹ and the complexing capacity was 4.4×10^{-8} mol g⁻¹. For Cd²⁺, a single linear adsorption with a slope of 515.1 ± 8.7 ml g⁻¹ was found. A decrease in the temperature resulted in greater adsorption for both Cd²⁺ and Pb²⁺. For Pb²⁺, an increase in the salinity resulted in a decrease of the adsorption. For Cd²⁺, the reverse behavior was observed as a consequence of a direct competition between the chitin surface groups and the Cl⁻ ions in solution. © 1990 Academic Press, Inc.

INTRODUCTION

The observed concentrations of many reactive trace elements in the oceans are recognized to be considerably lower than those calculated with respect to their least soluble salt (1). The scavenging of metals is an important mechanism that limits the concentration of certain trace elements in the oceans. A treatment of the adsorption properties of sinking particulate matter in the deep ocean has been given by Balistrieri *et al.* (2). These workers suggest that the adsorptive properties of marine particulate matter are controlled by organic coatings. Relatively little is known about the adsorptive characteristics of such organic films or coatings for trace metals (3). Hunter (4) has presented data showing that carboxylic acid and phenolic functional groups appear to be the major ionizable groups in such organic coatings. Scavenging in the ocean has been investigated for relatively few metals

(5–6). By contrast numerous laboratory studies have been carried out on the uptake of trace metals by sediments, pure mineral phases, and biological material (7–12).

Various functional groups, such as carboxylic, amino-, thio-, hydroxo- and hydroxycarboxylic, as well as relatively large surface areas are exhibited by phytoplankton cells, algae, biological debris, and bacteria. Taking into account these facts, biogenic organic particles play an important role in the binding of metals and their transfer to the sediment, thereby regulating the concentration of dissolved metals (12–20).

Chitin, as well as its deacetylated derivative chitosan, is a constituent of the natural dissolved and particulate organics and part of fungi and bacteria. Chitin-metal complexes are known to be biodegradable (21, 22). This makes chitin an important agent for metal transport. When the chitin-metal complexes break down, they release a large amount of those metals back into the seawater.

Most of the studies carried out using these natural polymers investigated possible uses of

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chitosan to remove metal ions in waste and natural water (23–31) due to its higher chelating ability. However, since chitin is a natural component of particulate organic material, it can serve as a model absorber of metals in ocean water (32).

In this paper we examine the adsorption of Cd^{2+} and Pb^{2+} to chitin in seawater. The measurements were made as a function of pH, salinity, and temperature and in the presence of competing metal ions in an attempt to better understand the mechanism of the adsorption.

EXPERIMENTAL

The chitin powder used was from crab shells and obtained from Sigma. Prior to use, the chitin was washed several times with 0.1 M HCl. After centrifugation at 12,000 rpm the chitin was eluted repeatedly with Millipore Super Q ion-exchanged water until the pH was constant. The samples were air-dried. Taking into account previous studies (23, 24, 32), the amount used in all the experiments was 6 g dm^{-3} of chitin. The surface area was measured by the BET method using krypton as the adsorbate. The value found was $0.5 \pm 0.03 \text{ mol}^2 \text{ g}^{-1}$ for the bulk chitin used in most of the experiments. Various size fractions from 88 to 210 μm gave similar values (to $\pm 0.05 \text{ mol}^2 \text{ g}^{-1}$). Preliminary studies with different fractions ranging from 250 μm to lower than 88 μm gave adsorption results similar to those of the bulk, which was used in all the following studies. Gulf Stream seawater ($S = 35.53$) was filtered through 0.45- μm Millipore acid-washed filters prior to use. Cadmium, lead, and copper atomic adsorption standard solutions from Sigma were used to make up the solutions.

Differential pulse anodic stripping voltammetry (DPASV) was used for all the metal determinations. The measurements were performed with the PAR 303 static drop mercury electrode (SDME) working in the hanging mercury drop electrode (HMDE) mode, using the PAR Model 348B polarographic analyzer system connected to a DMP-40 plotter. A

polyethylene cell was employed (33). A Ag/AgCl electrode was used as the reference electrode and a coiled platinum wire as the auxiliary electrode.

The reduction potential was -0.9 , -0.8 , and -0.6 V, respectively, for Cd^{2+} , Pb^{2+} , and Cu^{2+} . In all cases, the rate was 2 mV/s; the pulse height, 50 mV; and the deposition time, 1 min. For most of the studies, the measurements were made in duplicate.

The measurements of adsorption of Cd^{2+} and Pb^{2+} to chitin were made after the samples were equilibrated at the desired temperature in a shaker bath 24 h before its determination. The concentrations of metals in the samples were determined after filtration using HA Millipore acid-washed 0.45- μm filters. Every point represents the result of a separate run. The metals were analyzed in the filtrate by using the method of standard addition. The pH was adjusted by adding 0.1 M HCl or NaOH. All the pH measurements were made on the free proton scale (34) using Tris-seawater buffers.

RESULTS AND DISCUSSION

Uptake kinetics of Cd^{2+} and Pb^{2+} . The rapid uptake of Cd^{2+} and Pb^{2+} is shown in Fig. 1. Both metals reach the maximum adsorption in about the same time. Assuming a pseudo-

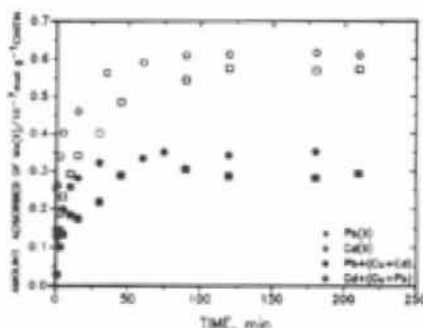


FIG. 1. Kinetics of Cd^{2+} and Pb^{2+} uptake to chitin in seawater (pH 8.2). The amount adsorbed of each metal in the absence and in the presence of other metals is plotted as a function of time. Initial concentration of each metal, $5 \times 10^{-7} \text{ M}$.

first order kinetic uptake of these metals, the half-times calculated are 20 ± 6 and 22 ± 5 min, respectively, for Cd^{2+} and Pb^{2+} . Chitin has a higher adsorption capacity for $\text{Cd}(\text{II})$ than for $\text{Pb}(\text{II})$. After the equilibration time, 73% of the initial amount of Cd^{2+} (5.0×10^{-7} M) was adsorbed on chitin while only 41% of initial Pb^{2+} (5.0×10^{-7} M) was adsorbed. These half-times and the percentages of metal adsorbed on chitin are in good agreement with the results obtained by Yang and Zall (31) for these metals in processing wastes. Taking into account the data published by these authors (32), the adsorptions follow the sequence $\text{Cu} > \text{Cd} > \text{Pb}$. This order shows a correlation with the second ionization potential, as exhibited by chitosan (23).

Adsorption isotherms. In Figs. 2 and 3, a typical determination of the complexation capacity of seawater is shown by curves 1 and 2 for both $\text{Pb}(\text{II})$ and $\text{Cd}(\text{II})$. A van den Berg-Ruzic plot (35) was used (Fig. 4).

$$\frac{[\text{Me}']}{[\text{RMe}]} = \frac{[\text{Me}']}{C_{Lr}} + \frac{1}{K'_{\text{cond}(\text{Me}')}C_{Lr}} \quad (1)$$

where $[\text{RMe}]$ is the concentration of metal ion bound to the surface expressed as mol g^{-1} (chitin dry wt), C_{Lr} is the total ligand concentration, and $K'_{\text{cond}(\text{Me}')}$ is the conditional

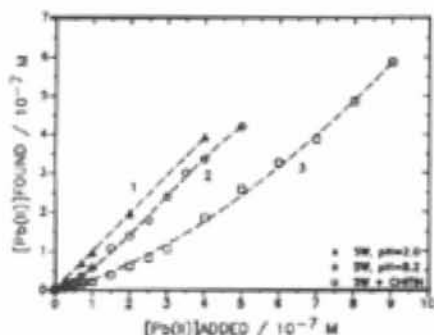


FIG. 2. Natural complexing capacity of seawater, calculated from curves 1 and 2, and increased complexing capacity by the addition of chitin, calculated from curves 1 and 3. The amount of lead is determined using curves 2 and 3.

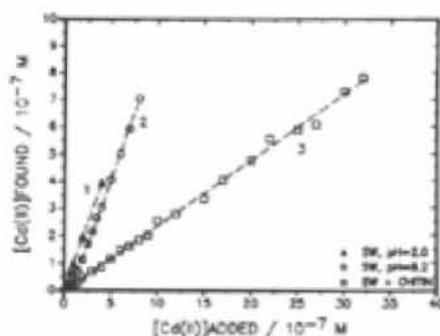


FIG. 3. Complexing capacity of seawater to Cd^{2+} in the absence of chitin, calculated using curves 1 and 2, and in the presence of chitin, calculated using curves 1 and 3. The amount of Cd^{2+} is determined using curves 2 and 3.

stability constant determined with respect to $[\text{Me}']$, the concentration of the metal ion in all its inorganic forms. The values obtained for the Gulf Stream seawater are shown in Table I. Again, higher ligand concentrations are exhibited by $\text{Cd}(\text{II})$ than by $\text{Pb}(\text{II})$ and both are lower than those of $\text{Cu}(\text{II})$. Similar values for the three compounds are obtained for the stability constants. This treatment assumes that metal complexation can be adequately represented by a single ligand and complexes having a 1:1 stoichiometry. The slight curvature observed at lower concentrations for

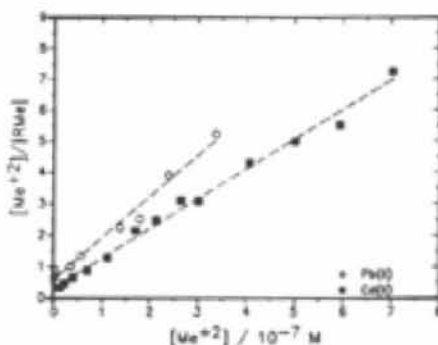


FIG. 4. Determination of the complexing capacity of Gulf Stream seawater from titration data for Cd^{2+} and Pb^{2+} according to Eq. (1).

TABLE I

Complexation Parameters Derived from a Single-Ligand Model Using the van den Berg/Ruzic Plot (35) for Gulf Stream Seawater

	β_n (M)	$\log K_{\text{overall}}$
Cd ²⁺	1.05×10^{-7}	7.5 ± 0.1
Pb ²⁺	7.59×10^{-8}	7.3 ± 0.1
Cu ²⁺	1.75×10^{-7}	$7.4 \pm 0.1^*$

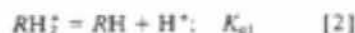
* Ref. (32).

Cd(II) is taken as an indication of the presence of two or more ligands of different stability constants (35). In both cases, only the linear relationship has been analyzed. The complexation parameters derived from the single-ligand model may not actually represent the ligand or binding sites in the sample. For a set of ligands with broadly similar stability constants, only an average stability constant will be obtained by this technique.

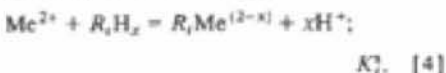
Figures 2 and 3 show the changes of the seawater's complexing capacity (curve 3) as a consequence of the addition of chitin. The adsorbed amount of cadmium and lead was estimated using curves 2 and 3, while the equilibration was obtained from curves 3 and 1.

An equilibration plot $\{RMe\}$ versus $\{Me(II)\}$ gives the adsorption isotherm. Figures 5 and 6 show the different adsorption isotherms for lead and cadmium, respectively.

A surface complex formation model can be used to describe the adsorption of lead to chitin surface groups. The chitin surface acid-base properties (32) may be characterized by



The metal complex formation with the chitin surface may be considered as that with polyfunctional macromolecules,



where R_n designates the deprotonated surface site. A general macroscopic adsorption

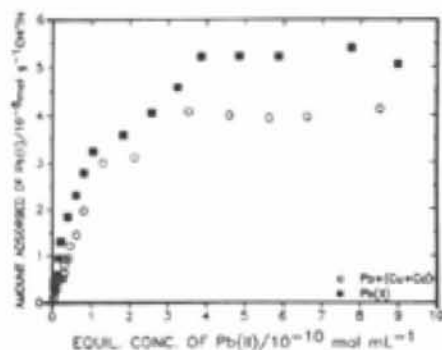
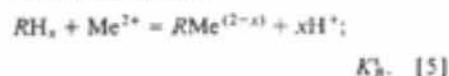


FIG. 5. Adsorption isotherm of Pb²⁺ and chitin in natural seawater. Data are plotted according to the Langmuir equation [8] both in the absence and in the presence of Cd²⁺ and Cu²⁺ at the same concentration of each metal added.

equilibrium involving various adsorption mechanisms is assumed, giving an average equilibrium constant



The equilibrium constant for Eq. [5] may be defined for a given pH, omitting the charges, in terms of a conditional constant as

$$K_8^H = \frac{\{RMe\}}{\{RH_n\}\{Me^{2+}\}} \quad [6]$$

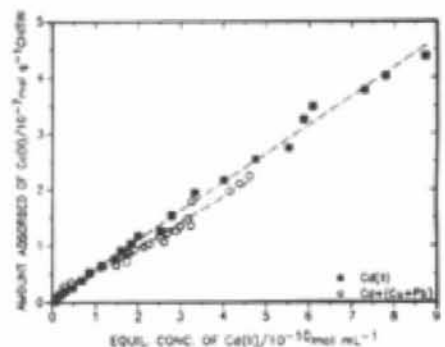


FIG. 6. Single adsorption isotherm exhibited by Cd²⁺ adsorbed to chitin both in the absence and in the presence of Cu²⁺ and Pb²⁺.

Equation [6] can also be interpreted in terms of a Langmuir isotherm,

$$\Gamma_{Me} = \frac{\Gamma_{max}[Me^{2+}]}{(K'_i)^{-1} + [Me^{2+}]} \quad [7]$$

or

$$\{RMe\} = \frac{\{R_T\}[Me^{2+}]}{(K'_i)^{-1} + [Me^{2+}]} \quad [8]$$

where $\{RMe\}$ and $\{R_T\}$ correspond to Γ_{Me} and Γ_{max} , respectively, and are the amount of metal ion adsorbed and the maximum value of the metal ion adsorption capacity (complexing capacity) $[\text{mol g}^{-1}]$; and K'_i is the conditional constant, valid for a given pH. Figure 5 shows the usual form of Langmuir isotherm (Eq. [8]) for the adsorption of lead to chitin. We may derive from the experimental data the equilibrium constant K'_i , transforming Eq. [8] into

$$\frac{1}{\{RMe\}} = \frac{1}{\{R_T\}} + \frac{1}{K'_i\{R_T\}} [Me^{2+}]^{-1} \quad [9]$$

and by plotting $\{RMe\}^{-1}$ vs $[Me^{2+}]^{-1}$, the values of $\{R_T\}$ and K'_i can be evaluated. Figure 7 illustrates such a plot for the binding of Pb^{2+} to chitin at pH 8.2. At high surface coverage, a deviation from the linear relationship is observed. This indicates that Pb^{2+} ions bind first to the highest affinity surface ligands and subsequently to those of less activity. The values obtained for the amount adsorbed at mono-

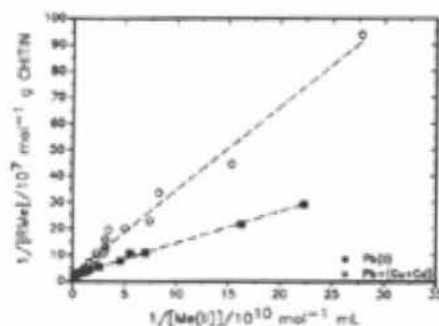


FIG. 7. Langmuir plot (Eq. [9]) for the binding of Pb^{2+} from titration data (Fig. 5).

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TABLE II

Binding Constants to the Surface of Chitin		
	R_T (mol g ⁻¹)	K'_i (ml mol ⁻¹)
Pb^{2+}	4.43×10^{-6}	$1.86 (\pm 0.2) \times 10^{10}$
Cd^{2+}		515.1 ± 8.7^a
Cu^{2+}	6.87×10^{-6}	$8.99 (\pm 0.90) \times 10^{10}$
$Pb + (Cu + Cd)^b$	3.88×10^{-6}	$8.07 (\pm 3.01) \times 10^9$
$Cd + (Cu + Pb)^c$		451.3 ± 12^a
$Cu + (Cd + Pb)^c$	5.88×10^{-6}	$9.62 (\pm 2.24) \times 10^{10}$

^a Values corresponding to linear isotherm.

^b Ref. 32.

^c Same amount of each metal was added.

layer capacity $\{R_T\}$ and for the conditional constant K'_i or Langmuir parameters are given in Table II. Using the $\{R_T\}$ value for Cu^{2+} of 6.86×10^{-6} mol g⁻¹ chitin given by Gonzalez-Davila and Millero (32), one finds that 150 times more copper than lead can be adsorbed on chitin producing a complete monolayer.

Figure 6 shows the linear isotherm for the adsorption of Cd(II) to chitin, indicating that K_p , the chitin/water partition coefficient, is constant and equal to the slope of the isotherm. Linear isotherms for the adsorption of cadmium on riverine-suspended particles also have been shown by Commans and van Dijk (36). The value obtained for K_p is 515.1 ± 8.7 ml g⁻¹ chitin. This kind of isotherm is shown by solutes that do not interact strongly with specific surface sites on the adsorbent (37), indicating a nonspecific interaction of cadmium on chitin.

Effects of pH, temperature, and salinity. The pH dependence of the Pb^{2+} and Cd^{2+} adsorption on chitin has been studied by measuring the residual solute concentrations by DPASV in the filtrate. Adsorption of metal ions at the solid chitin surface-water interface is strongly pH-dependent (Fig. 8), because the properties of both the chitin surface (charge and potential) and the solution composition (metal ion speciation) change with pH.

Figure 8 shows the effect of pH on the adsorption of Pb^{2+} and Cd^{2+} on chitin. At pH

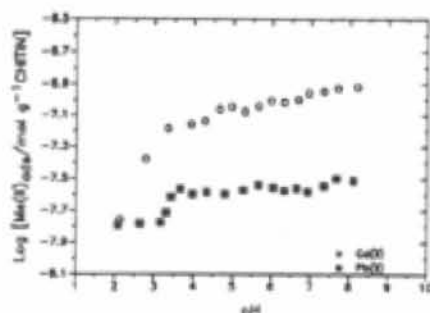


FIG. 8. Effect of pH on the adsorption of $1 \mu\text{M Cd}^{2+}$ and $0.5 \mu\text{M Pb}^{2+}$. The pH of seawater was adjusted by addition of NaOH or HCl.

values lower than 3.5, little adsorption of Pb^{2+} on chitin occurs; at values of pH above 3.5, a nearly constant amount of Pb^{2+} is adsorbed. The hydroxo complexes of $\text{Pb}(\text{II})$, such as PbOH^+ , in our opinion, are fully labile, because change in the peak potential E_p at pH near 7 is due to the formation of a hydroxo complex of $\text{Pb}(\text{II})$ (38).

For Cd^{2+} , at pH values between 2 and 3.2, the amount of Cd^{2+} adsorbed increases with a slope of 0.58 ± 0.2 . At pH values higher than 3.2, a slight increase with a slope of 0.06 ± 0.1 in the adsorbed Cd^{2+} concentration is exhibited. Over all ranges of pH studied, the chitin results are similar to those found by Murray (39), Morgan and Stumm (40), and Laitinen and Zhou (41) for different elements adsorbed to MnO_2 .

These results do not correspond with Eq. [12] below. Neglecting the activity coefficient, the mass law expression for the reaction [5] is

$$K_b^* = \frac{\{R\text{Me}\}\{H^+\}^n}{\{RH_n\}\{Me^{+2}\}} \quad [10]$$

Upon rearrangement we have

$$\log \frac{\{R\text{Me}\}}{\{Me^{+2}\}} = Z + n \text{pH}, \quad [11]$$

where $Z = \log K_b^* + \log \{RH_n\}$. If Z is considered a constant, Eq. [11] becomes

$$\log \frac{\{Me(\text{II})\}_{\text{ads}}}{\{Me(\text{II})\}_{\text{tot}}} = Z + n \text{pH}. \quad [12]$$

Equation [5] predicts a slope of 2 for the adsorption of divalent metals to chitin, whereas the slopes shown in Fig. 8 are only 0.45 ± 0.1 and 0.57 ± 0.2 , respectively, for Pb^{2+} and Cd^{2+} . Similarly, the pH dependence of the adsorption of other metal ions (32, 39–41) was always much less than 2 and closer to the value 0.5. As has been observed by others (32, 39–41), the cause of the difference between the slope and the ratio may be that the values of Z in Eq. [12] may not be constant even if the amounts of Pb^{2+} or Cd^{2+} adsorbed are very small. Different sites may exist on the surface of chitin which may be changed by the solution. The values obtained for the amphoteric properties of the surface of chitin in 0.7 M NaCl were $\text{p}K_{a1} = 4.4 \pm 0.2$ and $\text{p}K_{a2} = 6.4 \pm 0.3$ (32). The number of $-\text{SO}^-$, $-\text{SOH}$, and $-\text{SO}_2^-$ sites on the surface of chitin may change with varying pH. The low values may also be due to the adsorption of anions as counterions and the chemisorption of anions by replacement of OH^- groups. Either of these processes would change the $\text{H}^+/\text{Me}^{2+}$ ratio and the cation adsorption equilibrium.

The effect of temperature on the adsorption of cadmium and lead on chitin is shown in Fig. 9. In both cases, the adsorption on chitin decreases at higher temperatures, showing the same behavior as the adsorption of gases on solids. The specific energy E was calculated for the adsorption of Cd^{2+} and Pb^{2+} using

$$K_p = A \exp(-E/RT), \quad [13]$$

where A is the frequency factor and K_p is the partition coefficient of Cd^{2+} or Pb^{2+} on chitin. The linear fits of the values of $\ln K_p$ versus $1/T$ (K) shown in Fig. 9 give values of $E_{\text{Cd}} = -2.06 \pm 0.45 \text{ kcal/mol}$ and $E_{\text{Pb}} = -5.26 \pm 0.62 \text{ kcal/mol}$. These negative specific adsorption energies of $\text{Cd}(\text{II})$ and $\text{Pb}(\text{II})$ may be due to the heat of hydration of these metals being lower than their heat of adsorption.

Salinity influences adsorption due to effects on adsorbate activities in solution, as well as

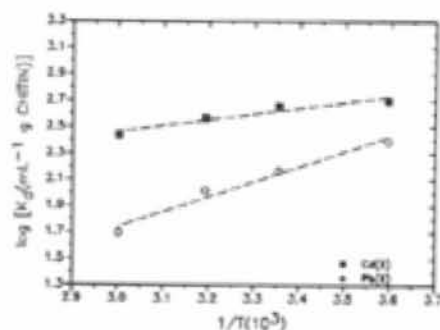


FIG. 9. Arrhenius plot (Eq. [13]) for the dependence of temperature on the adsorption of 5×10^{-5} M Cd²⁺ and 5×10^{-5} M Pb²⁺ to chitin in seawater; pH 8.2; time of adsorption, 24 h.

surface charge and double-layer properties of the hydrated particles. The effect of salinity on the partition coefficient of Pb²⁺ and Cd²⁺ is shown in Fig. 10. A linear relationship between $\log K_p$ and $S^{1/2}$ is found in both cases. For lead, the slope of $\log K_p$ with $S^{1/2}$ increases with a slope of 0.1. For cadmium, the amount adsorbed decreases when salinity increases, with a slope of -0.12 . The same results have been shown by Comans and van Dijk (36) for the Cd²⁺ adsorption on riverine-suspended particles in fresh water and in more saline water. At very low salinities, most of the cadmium will be present as Cd²⁺, but when the salinity increases, the formation of stable Cd-chloro complexes occurs and dominates the cadmium speciation. It can be concluded that the adsorption behavior of cadmium is regulated by the decreasing free Cd²⁺ activity in solution, through the combined effect of increasing cadmium complexation (mainly by Cl⁻) and increasing ionic strength. This suggests that the free Cd²⁺ activity determines the partition of cadmium between the chitin and the solution. The system can be described as a direct competition for Cd²⁺ ions between ligands at the chitin surface and Cl⁻ in the solution. These chloride complexation effects give a metal distribution that can be described by a single adsorption isotherm (Fig. 6).

Competition with other metals. In natural

aqueous systems several metallic ions will be present, and a selective uptake of these ions by chitin surface groups can be expected. In order to investigate this effect, a mixture containing Cu²⁺, Cd²⁺, and Pb²⁺ was added.

Figure 1 shows the effect of added Cu²⁺ on the uptake rate for both Cd²⁺ and Pb²⁺. Lower equilibrium concentrations of each metal are achieved. The Cd²⁺ concentration changes from 73 to 69% while the Pb²⁺ concentration changes from 41 to 35%. The half-time calculated assuming a pseudo-first order uptake changes from 20.5 ± 6.2 to 28.6 ± 5.4 min for Cd²⁺ and from 22.6 ± 5.1 to 33.5 ± 6.1 min for Pb²⁺. Since Cu²⁺ has a higher affinity for chitin surface groups (32), the highest affinity surface groups of chitin are rapidly occupied by Cu²⁺. The adsorption of metal ions by chitin and chitosan from mixed metal ions solution, shown by Muzzarelli (24) and Yoshinari and Subramanian (21), does not follow a set stoichiometry. This suggests that there may be more than one active site for different metals on the surface of these polymers.

Figures 5 and 7 show the effect of the presence of Cu²⁺ and Cd²⁺ on the adsorption isotherm of Pb²⁺ on chitin. When higher amounts of other metals are added, a lower concentration of Pb²⁺ is adsorbed. The values obtained for the Langmuir parameters calcu-

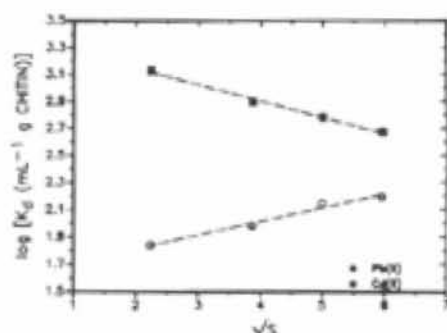


FIG. 10. Effect of salinity on the adsorption of $0.5 \mu\text{M}$ Cd²⁺ and $0.5 \mu\text{M}$ Pb²⁺ to chitin. Linear relations are observed for both metals as a function of $S^{1/2}$.

lated using the transformed Langmuir equation (Eq. [9]) are shown in Fig. 7 and given in Table II ($K_{11} = 5.50 \times 10^{-9} \text{ mol g}^{-1}$). The complexing capacity for Pb^{2+} was $50 \times 10^9 \text{ mol g}^{-1}$ less in the presence of copper and cadmium than without these metals. The small changes in the conditional constant shows that the sites occupied by Pb^{2+} are the same.

In Fig. 6, a slightly lower K_p partition coefficient is observed in the presence of Cu^{2+} and Pb^{2+} for the adsorption of Cd^{2+} (Table II), mainly due to the presence of the Cu^{2+} ion.

CONCLUSION

It has been demonstrated that cadmium and lead can be adsorbed by chitin surface groups in seawater. The adsorption of lead on chitin can be correlated well with surface complex formation equilibria, while the experimental data for the adsorption equilibrium of Cd^{2+} shows a single adsorption isotherm. Variations in factors such as pH, temperature, and salinity have additional (positive or negative) effects on the mobilization of lead and cadmium. It is concluded that the Cd^{2+} activity is reduced by chloride complexation. The system can be described as a direct competition for Cd^{2+} ions between chitin surface groups and Cl^- in solution. When two or more transition metal ions are present together in the solution, Cu^{2+} , which forms the most stable complex with the polymer, is preferentially adsorbed, leaving part of the Cd^{2+} and Pb^{2+} in solution. Our results suggest, however, that there may be more than one active site for the different metals on the surface of chitin.

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