

## The adsorption of copper to chitin in seawater

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**Abstract**—The interaction of metal ions with particulate matter is important in limiting their concentration in seawater. Chitin is one of the constituents of the natural particulate organic matter that can interact with metal ions and therefore may serve as a reasonable model for natural organic solids. The adsorption of  $\text{Cu}^{2+}$  on the chitin surface has been studied in seawater as a function of pH, temperature, and salinity. The amphoteric properties of the surface of chitin were characterized in 0.7 M NaCl in terms of a two-protonic acid-base system ( $\text{pH}_{\text{PZC}} = 5.4$ ) with acidity constants  $p^*K_{a1}^* = 4.4 \pm 0.2$  and  $p^*K_{a2}^* = 6.4 \pm 0.2$ . The maximum proton exchange capacity of chitin was found to be  $2.3 \pm 0.3 \text{ mol kg}^{-1}$ , broadly similar to other solids. The rates of the adsorption were quite rapid ( $t_{1/2} = 8 \text{ min}$ ) and not strongly affected by the presence of other metals such as  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ . The adsorption equilibrium data have been found to correlate well with surface complex-formation equilibria or the mathematically equivalent Langmuir-type adsorption equilibria. The value for the stability constant of  $\text{Cu}^{2+}$  on chitin was found to be  $\log^* K_{\text{c}}^* = 8.95 \pm 0.01$ , and the complexing capacity of chitin was found to be 6.9 and  $5.9 \mu\text{mol g}^{-1}$ , respectively, in the absence and in the presence of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ . An increase in the salinity and a decrease in the temperature result in greater adsorption of  $\text{Cu}^{2+}$  to chitin.

### INTRODUCTION

THE SCAVENGING OF trace metals by particulate matter is important in regulating the concentration and distribution of metals in the oceans (WHITFIELD and TURNER, 1987). Field measurements suggest that the scavenging process of some metals can be characterized as a reversible equilibrium, although kinetics may also be significant (BACON and ANDERSON, 1982; NYFFELER et al., 1986; NOZAKI et al., 1987; HONEYMAN and SANTSCHI, 1988). Although few studies of scavenging processes of metals have been made in the field (SOMAYAJULU and CRAIG, 1976; ANDERSON et al., 1983), numerous laboratory studies have been carried out on the uptake of metals by sediments and pure mineral phases (DUGGER et al., 1964; HUANG and STUMM, 1973; MURRAY and BREWER, 1977; BENJAMIN and LECKIE, 1981; BALISTRERI and MURRAY, 1982; DAVIS 1984; DAVIS and LECKIE, 1979). A great deal of emphasis has been placed on the adsorption behavior of iron and manganese oxides, because their presence in marine sediments and ferromanganese nodules is thought to be responsible for controlling certain trace metal concentrations in seawater.

Moreover, it is now widely accepted that adsorption and complexation of trace metals by natural dissolved and particulate organic materials is a critical factor that influences both bio-availability and toxicity to organism (GONCALVES and LOPES DA CONCEICAO, 1989; COALE and BRULAND, 1988). An understanding of the interactions between the metals ( $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ , etc.) and natural heterogeneous compounds such as organic macromolecules (e.g., humic substances, chitin, chitosan, amino acids, etc.) and exopolymers from bacteria or algae is indispensable for determining the behavior of these cations in aqueous environ-

ments ranging from rivers, lakes, and seawater to soil and sediment pore waters (DAVIS, 1984).

Phytoplankton cells, algae, biological debris, and bacteria exhibit in these systems relatively large surface areas containing various functional groups—such as carboxylic, amino-, thio-, hydroxo-, and hydroxy-carboxylic—that can interact with metal ions. These biogenic organic particles play an important role in binding metals and transferring them to the sediment, thereby regulating the concentration of dissolved metal ions (FISHER, 1985; FISHER et al., 1980, 1983, 1984, 1987; XUE et al., 1988; SCHREIBER et al., 1985; GORDON and MILLERO, 1987; GONCALVES and LOPES DA CONCEICAO, 1989).

Chitin, its deacetylated derivative chitosan, and humic substances have the ability to complex a number of transition elements in natural aqueous systems. Chitin and chitosan are constituents of the natural dissolved and particulate organics and part of fungi and bacteria. They are consequently abundant in the natural environment. Since chitin is rapidly biodegraded (ZOBELL and RITTENBERG, 1983), it is not a major component of sediments. While chitosan and chitin can form stable metal complexes, one would expect the complexes to also be biodegradable. This may make chitin an important agent for transporting metals from surface to deep waters. The complexes could be formed in surface waters, sink, and be degraded in deep waters, releasing the associated metals (YOSHINARI and SUBRAMANIAN, 1976; SUBRAMANIAN, 1978).

Much of our knowledge of the interactions of chitins with metals comes from investigations of their possible uses to remove heavy metals in waste and natural waters (MUZZARELLI, 1973, 1977; HUNG and HAN, 1977; EDIN et al., 1980; SUDER and WIGHTMAN, 1983; YANG and ZALL, 1984). Chitosan was studied due to its high chelating ability (MUZZARELLI, 1973, 1977; MUZZARELLI et al., 1980; MUZZARELLI and TANFANI, 1982; KURITA et al., 1979). Since chitin is a

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natural component of particulate organic material, it can serve as a model organic phase for studying metal adsorption in marine systems.

In this paper we examine the adsorption of  $\text{Cu}^{2+}$  to chitin in seawater. The measurements were made as a function of pH, salinity, and temperature in an attempt to better understand the mechanism of the adsorption.

### EXPERIMENTAL

The chitin powder used (Sigma) was derived from crab shells. Prior to use, the chitin was washed three times with 0.1 M HCl. The solid and solution were separated by centrifugation at 12,000 rpm for 15 min and then eluted repeatedly with Millipore Super Q ion-exchanged water until the pH was constant. The samples were air dried. The surface was measured by the BET method using krypton as the adsorbate. The value found was  $0.5 \pm 0.03 \text{ m}^2 \text{ g}^{-1}$  for the bulk chitin used in most of the experiments. Various size fractions from 88  $\mu\text{m}$  to 210  $\mu\text{m}$  gave similar values (to  $\pm 0.1 \text{ m}^2 \text{ g}^{-1}$ ). Chitin powder was sieved prior to study using pre-washed Nylon mesh. Preliminary studies with different fractions ranging between 250  $\mu\text{m}$  to lower than 88  $\mu\text{m}$  gave similar adsorption results as the bulk, which was used in all the following studies. The concentration used in all the experiments was  $6 \text{ g dm}^{-3}$  of chitin, an amount which is similar to that used by MUZZARELLI (1973, 1977). Similar results were exhibited using different amounts of chitin (MUZZARELLI, 1977). Gulf Stream seawater ( $S = 35.53$ ) was filtered through 0.45  $\mu\text{m}$  Millipore acid-washed filters. Copper, Cadmium, and Lead atomic absorption standard solutions (Sigma) were used to make up the solutions.

The metal concentrations were determined using Differential Pulse Anodic Stripping Voltammetry (DPASV). The measurements were performed with the PAR 303 Static Drop Mercury Electrode (SDME) using the PAR Model 348B Polarographic Analyzer System connected to a DMP-40 plotter. For all the measurements performed in the Hanging Mercury Drop Electrode (HMDE) mode, a polyethylene cell was employed (SIPOS et al., 1974). An Ag/AgCl electrode was used as the reference electrode and a coiled platinum wire as the auxiliary electrode.

The reduction potential was  $-0.6$ ,  $-0.8$ , and  $-0.9 \text{ V}$ , respectively, for  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cd}^{2+}$ . In all cases, the purge time was 5 min; the scan rate, 2 mV/s; the pulse height, 50 mV; deposition time, 1 min. For most of the studies, the measurements were made in duplicate. The peak potential of Copper(II), Lead(II), and Cadmium(II) are, respectively,  $-0.180 \pm 0.02$ ,  $-0.470 \pm 0.01$ , and  $-0.680 \pm 0.005 \text{ V}$ .

The measurements of adsorption of  $\text{Cu}^{2+}$  to chitin were made after the samples were equilibrated overnight at the desired temperature in a shaker bath. All the samples were equilibrated with room air at the given pH, temperature, and salinity studied. The pH was adjusted by adding 0.1 M HCl or NaOH. All the measurements were made on the free proton scale (MILLERO, 1986). The seawater pH measurements were calibrated using TRIS-seawater buffers. The concentrations of metals in the samples were determined after filtration using HA Millipore acid-washed 0.45  $\mu\text{m}$  filters. The metals were analyzed in the filtrate by using standard additions.

The values of the  $pK_a^*$  of the surface sites of chitin were determined from potentiometric titrations in 0.7 M NaCl solutions with 1 M HCl and NaOH. The titrations were carried out in a 200  $\text{cm}^3$  water-jacketed cell controlled to  $25 \pm 0.05^\circ\text{C}$ . The titrations were made with the titrator system used in our earlier studies (THURMOND and MILLERO, 1982). The system is automated and controlled with an Apple II computer. The emf of the glass pH electrode (Ross\*) and Calomel reference electrode was measured with a Metrohm 605 pH meter. The emf is related to the concentration of the proton by

$$E = E^* - (RT/F) \ln [H^+] \quad (1)$$

where  $E^*$  is the apparent emf in the medium; and  $R$ ,  $T$ , and  $F$  have their usual meanings. The values for  $E^*$ , the stoichiometric ionization constants  $K_a^*$ , and the cation exchange capacity were determined from the titrations using a non-linear least-squares program (ARENA et al., 1978). A typical titration of chitin is shown in Fig. 1.

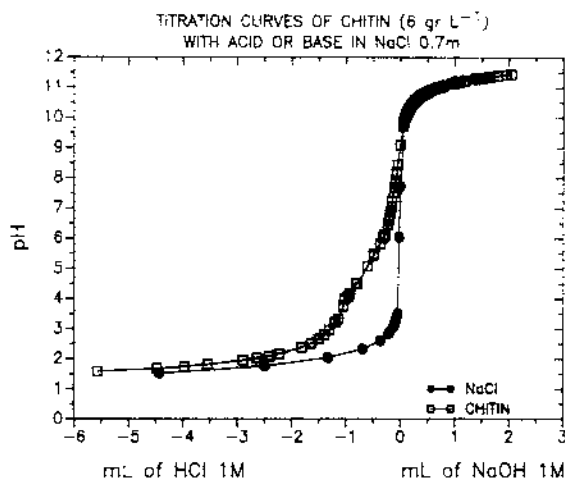
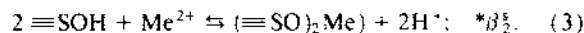


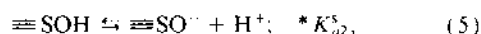
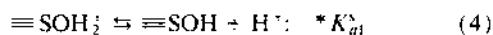
FIG. 1. Titration curve of chitin with HCl or NaOH in 0.7 M NaCl at  $25^\circ\text{C}$ .

### RESULTS AND DISCUSSION

The adsorption of metal ions by oxide surfaces has been represented by the formation of surface complexes (STUMM and MORGAN, 1981) using equilibria of the type

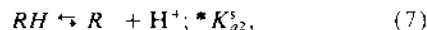
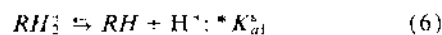


The acid-base properties of the surface functional groups may be characterized as a diprotic acid

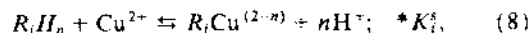


where  $\equiv\text{SOH}_2$  is a positively charged surface group with two dissociable protons,  $\equiv\text{SOH}$  is a neutral surface group with one dissociable proton, and  $\equiv\text{SO}^-$  is a negatively charged surface group. The values of  $*K_{a1}^*$  and  $*K_{a2}^*$  are the conditional acidity constants of the positively and negatively charged surface groups. The equilibrium constant for Eqns. (2) to (5) for a given ionic media have been shown (STUMM and MORGAN, 1981; SPOSITO, 1983; BUFFLE and ALTMANN, 1987) to depend on the charge on the surface and the extent of surface binding of metal ions and protons.

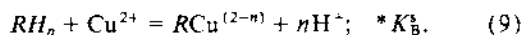
Since the chitin surface contains various functional groups, this simple approach may not be appropriate. The acid-base properties may be characterized by the general equations



where  $RH_2^+$  and  $RH$  represent protonated surface sites, and where  $RH_2^+$  and  $RH$  are not necessarily the same groups. The adsorption of  $\text{Cu}^{2+}$  with the chitin surface may be more similar to the formation of  $\text{Cu}^{2+}$  complexes with polyfunctional macromolecules (XUE et al., 1988), the general equation being



where  $R_i$  represents a deprotonated surface site. Since the surface groups are not identical, it is not possible to determine all the values of  $*K_B^s$ . If one assumes that a general macroscopic adsorption equilibrium can be used to define an average equilibrium constant, we have



If the charges on the species are omitted, the equilibrium constant for Eqn. (9) is given by

$$*K_B^s = \frac{\{RCu\}\{H^+\}^n}{\{RH_n\}\{Cu^{2+}\}}, \quad (10)$$

where  $\{RCu\}$  and  $\{RH_n\}$  are, respectively, the copper and protons adsorbed to the chitin as mol g<sup>-1</sup>. For a given pH, the conditional constant is defined by

$$*K_H^s = \frac{\{RCu\}}{\{RH_n\}\{Cu^{2+}\}} \quad (11)$$

It should be noted that Eqn. (11) is mathematically and conceptually equivalent to the Langmuir isotherm

$$\Gamma_{Cu} = \frac{\Gamma_{MAX}[Cu^{2+}]}{(*K_H^s)^{-1} + [Cu^{2+}]} \quad (12)$$

or

$$\{RCu\} = \frac{\{R_T\}[Cu^{2+}]}{(*K_H^s)^{-1} + [Cu^{2+}]}, \quad (13)$$

where  $\{RCu\}$  and  $\{R_T\}$  correspond to  $\Gamma_{Cu}$  and  $\Gamma_{MAX}$ , the amount of copper adsorbed, and the maximum copper value of ion adsorption capacity or complexing capacity (mol g<sup>-1</sup>). The values of  $*K_H^s$  and  $\{R_T\}$  can be obtained by using typical Scatchard or Langmuir plots. Although this is a simplistic approach of modelling the complex adsorption of copper and other metals to chitin, it gives a chemical framework to evaluate our results.

#### Acid-base properties of chitin

In our first series of measurements, an attempt was made to characterize the functional groups of chitin. Chitin is a polymer of *N*-acetylglucosamine; thus, chitin is an amide of acetic acid. However, chitin cannot be sharply distinguished from chitosan, because fully acetylated and fully deacetylated chitins do not normally occur in nature and are difficult to prepare (MUZZARELLI, 1977).

The acidity constants for chitin from Eqns. (6) and (7) are given by

$$*K_{a1}^s = \frac{\{RH\}[H^+]}{\{RH_2^+\}} \quad (14)$$

$$*K_{a2}^s = \frac{\{R^-\}[H^+]}{\{RH\}} \quad (15)$$

The sequential binding of protons by the various functional groups of the surface of chitin is shown in Fig. 1. The acidity constants involved in this titration have been determined by using the ACBA program (ARENA et al., 1978). Values of  $p*K_{a1}^s = 4.40 \pm 0.23$  and  $p*K_{a2}^s = 6.45 \pm 0.25$  were obtained as a result of different titrations of chitin in 0.7 M NaCl. The

pH of zero charge,  $pH_{PZC}$ , is a convenient reference value for characterizing surface charge, even though no surface group has a unique  $pH_{PZC}$ . Analytically,  $pH_{PZC}$  can be calculated from the pH at which  $\{RH_2^+\} = \{R^-\}$  or from Eqns. (14) and (15):

$$pH_{PZC} = \frac{1}{2}(pK_{a1}^s + pK_{a2}^s). \quad (16)$$

A value of  $pH_{PZC} = 5.38 \pm 0.2$  was found for chitin. At pH values below the zero point of charge,  $\{RH_2^+\} > \{R^-\}$ , and at pH values above  $pH_{PZC}$ ,  $\{R^-\} > \{RH_2^+\}$ . The maximum titratable proton exchange capacity of the chitin surface groups was found to be  $2.34 \pm 0.3$  mol kg<sup>-1</sup> chitin.

Table 1 shows values for the acidity constant of different adsorbents together with values of  $pH_{PZC}$ . A two-protic acid-base system has been used to interpret the acid-base properties for an algal surface by XUE et al. (1988). They interpreted the algal surface to contain carboxylic acid groups that deprotonate at pH 4–5 and amino groups that undergo proton transfer around pH 8–9.5 (comparable to the  $pK$  value of glycine  $pK_{a2} \approx 9.5$ ) (Table 1). Chitosan has been described as a strong base with a  $pK_a = 6.3$  (MUZZARELLI, 1973) corresponding to its primary amino groups (Table 1). The values that we obtained in this work are generally similar to the values for other organic and inorganic solids. The chitin surface can be interpreted from the titration curve (Fig. 1) as a surface containing primarily carboxylic acid groups with  $pK_{a1} = 4.40$ , which is comparable with the second acidity constant of phthalic acid  $pK_a \approx 5$ , and amino groups with a  $pK_a = 6.45$ . The latter value corresponds with the  $pK_a$  for the primary amino groups in the deacetylated derivative chitosan (Table 1).

#### Surface uptake of Cu<sup>2+</sup> by chitin

In Fig. 2, a typical determination of the complexing capacity of seawater is shown by curves 1 and 2. Using a van den Berg-Ruzic plot (APTE et al., 1988), the complexing capacity of seawater can be evaluated (Fig. 3):

$$\frac{\{Cu'\}}{\{CuL\}} = \frac{\{Cu'\}}{C_L} + \frac{1}{K'_{cond}(Cu')C_L}, \quad (17)$$

where  $C_L$  is the total ligand concentration in seawater and  $K'_{cond}(Cu')$ , the conditional stability constant determined with respect to  $[Cu']$ , the concentration of dissolved copper in all inorganic forms. The presence of two ligands or sites with sufficient affinity for Cu<sup>2+</sup> has been shown to cause the non-linear behavior of the plots (VAN DEN BERG, 1984). The cur-

Table 1. Acidity constants of surface groups (25°C).

Reactive group	Solid phase	Electrolytic solution	$pK_{a1}$	$pK_{a2}$	$pH_{PZC}$	Reference
Al-OH	$\gamma\text{-Al}_2\text{O}_3$	0.1M NaNO <sub>3</sub>	6.51	8.43	7.5	1
	$\gamma\text{-Al}(\text{OH})_3$	3.0M NaClO <sub>4</sub>	8.9	9.5		2
Si-OH	Silica gel	0.1M NaClO <sub>4</sub>		6.8		2
		0.5M NaClO <sub>4</sub>		7.2		2
Ti-OH	Anatase	3.0M NaClO <sub>4</sub>	4.98	7.8	6.4	2
Mn-OH	Mn <sub>2</sub> O <sub>3</sub> ·H <sub>2</sub> O	0.1M NaNO <sub>3</sub>		6.8		1
	MnO <sub>2</sub>	1.0M NaCl			1.5	3
----	Algae	0.1M KNO <sub>3</sub>	~4.5	~9		4
----	Chitosan	1M		6.3		5
----	chitin	0.7M NaCl	4.40	6.45	5.4	this work

1. HUANG and STUMM, 1973; 2. SCHINDLER and GAMSJAGER, 1972; 3. BALISTRERI and MURRAY, 1982; 4. XUE et al., 1988; 5. MUZZARELLI, 1973.

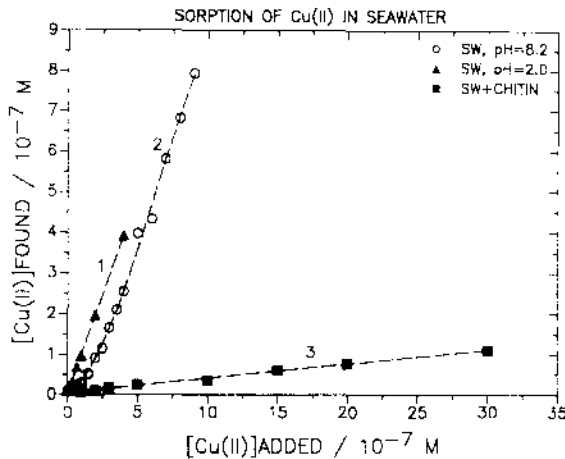


FIG. 2. The natural complexing capacity of Cu(II) in seawater.

vature in Fig. 3 at lower concentrations of Cu<sup>2+</sup> may be due to a second ligand. Our measurements are not sufficient in the low concentration to evaluate the first stability constant. The ligand concentration obtained for the Gulf Stream seawater is C<sub>L2</sub> = 175 nM, the same order of magnitude as found by others (see Table 2). In order to compare our conditional stability constant K'cond(Cu<sub>2</sub>) with other values reported by different authors (Table 2), it is necessary to use a conditional stability constant of the form K'cond(Cu<sup>2+</sup>), determined with respect to the free Cu<sup>2+</sup>:

$$[Cu^{2+}]_f = \frac{[Cu']}{\alpha_{Cu}} \quad (18)$$

α<sub>Cu</sub> is the inorganic side reaction coefficient of copper in seawater. Although sizable variability in the accepted inorganic side reaction coefficient for copper has been reported (COALE and BRULAND, 1988), a value of 24 (BYRNE and MILLER, 1985) was chosen to normalize our conditional stability constant with respect to free Cu<sup>2+</sup> in Table 2. The conditional value for log K'cond(Cu<sub>2</sub>) obtained is 7.4 ± 0.1 which corresponds with a normalized value of log K'cond(Cu<sup>2+</sup>) = 8.8 ± 0.2.

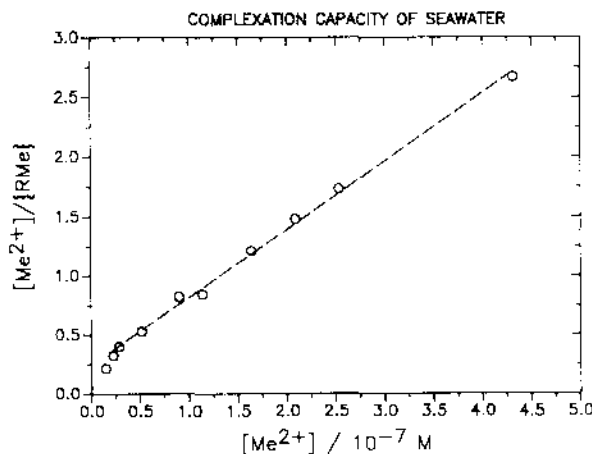


FIG. 3. Graphical treatment according to Eqn. (7) for the determination of the complexing capacity of Gulf Stream seawater from titration data.

Table 2. Values for copper-complexing ligands in seawater:

Location	[L <sub>1</sub> ](nM)	[L <sub>2</sub> ](nM)	logK <sub>1</sub> *	logK <sub>2</sub> *	Reference
GW Atlantic	1	24	9.2	9.8	1
Atlantic	11	23	12.5	10.6	2
Atlantic	51	85	10.3	9.4	3
Atlantic	4.96	23.93	10.7-12.4	8.3-9.1	4
S. Atlantic	1	20.25	12.5	9.1-10.0	5
S. Pacific	1.8	7.4	12.5	9.5-10.3	5
Gulf Stream	1.7	1.7	12.5	8.28	this paper

These values have been normalized to a common inorganic side reaction coefficient for copper of 24 (BYRNE and MILLER, 1985). They represent stability constants with respect to free copper, Cu<sup>2+</sup>.  
 1. SUNDA and FERGUSON, 1983; 2. van den BERG, 1984;  
 3. van den BERG et al., 1984; 4. BUCKLEY and van den BERG, 1986;  
 5. KRAMER, 1986; 6. COALE and BRULAND, 1988.

This value for the conditional stability constant of Cu<sup>2+</sup> in Gulf Stream seawater is in good agreement with those reported in Table 2 for Atlantic and Pacific seawaters. One must keep in mind that this simple treatment of the Cu<sup>2+</sup>-organic interactions does not necessarily prove that only two ligand sites are present. It should be considered to be a convenient way of accounting for the interactions.

It is obvious from Fig. 2 that the addition of chitin (curve 3) dramatically changes the seawater's complexing capacity. For its calculation, the adsorbed amounts of copper are estimated using curves 2 and 3, while the equilibria are obtained from curves 3 and 1. The adsorbed copper calculated in this manner was found to be in good agreement with the values measured on filtered samples.

Figure 4 shows Langmuir's isotherm [Eqn. (13)] for the adsorption of Cu<sup>2+</sup> on chitin. We may derive from the experimental data the equilibrium constant \*K<sub>H</sub><sup>+</sup>, transforming the Eqn. (13) into

$$\frac{1}{\{RCu\}} = \frac{1}{\{R\}} + \frac{1}{*K_H^+ \{R\} [Cu]} \quad (19)$$

and by plotting {RCu}<sup>-1</sup> vs [Cu<sup>2+</sup>]<sup>-1</sup> the values of {R} and \*K<sub>H</sub><sup>+</sup> can be evaluated. Equation (19) is mathematically equivalent to Eqn. (17).

Figure 5 illustrates such a plot for the Cu<sup>2+</sup> binding to chitin at pH 8.2. At high copper concentrations the data show deviations from the linear relationship. This may be due to

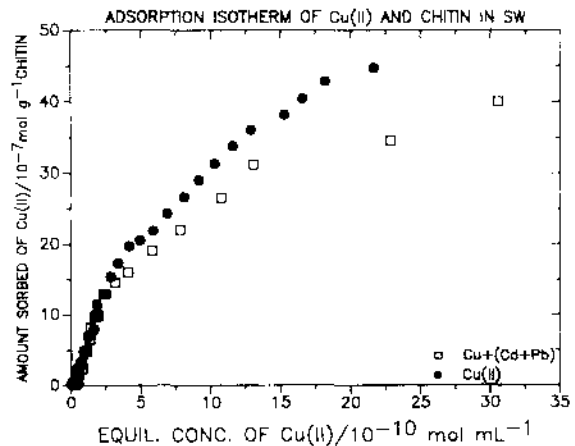


FIG. 4. Adsorption isotherm of Cu(II) on chitin in seawater (S = 35%) at 25°C in presence and absence of Cd(II) and Pb(II).

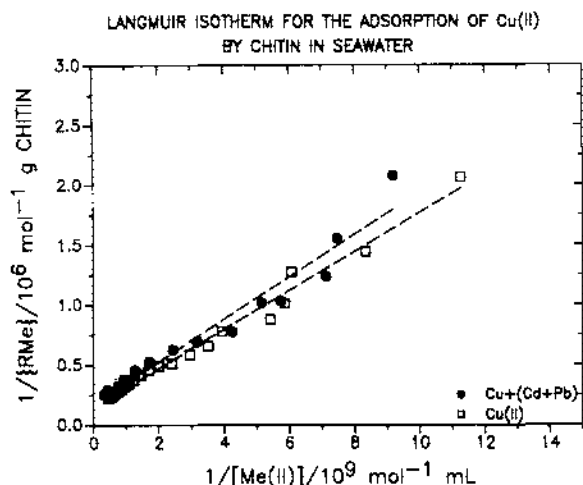


FIG. 5. Langmuir plot (Eqn. 18) for the binding of Cu(II) to chitin surface in seawater, pH = 8.2 and 25°C.

the occupation of different binding sites. The strength of Cu<sup>2+</sup> binding decreases with an increased copper loading of the chitin surface. This indicates that Cu<sup>2+</sup> ions become bound first to the highest affinity surface ligands and subsequently to those of lesser activity. The equilibrium constant as well as the maximum amount of adsorbed material required to give a complete monolayer on the chitin surface evaluated from the low surface coverage are given in Table 3, together with the values given by XUE et al. (1988) for the binding of Cu<sup>2+</sup> to algal surface. The surface sites on chitin are about ten times less than the sites on algae surface. The strength of the binding of Cu<sup>2+</sup> to chitin, however, is 100 times greater than for algae.

It has been pointed out by many workers (YANG and ZALL, 1984; XUE et al., 1988; GONCALVES and LOPES DA CONCEICAO, 1989) that there is no simple, fully rational model available to account for the surface complex formation on a system able to adsorb metals. The \*K<sub>H</sub><sup>2</sup> values are equilibrium quotients capable of expressing the average effect of metal ion binding to a mixture of chitin surface ligands and are valid only within certain conditions. The fitting of the data does not prove the validity of the model used.

*Uptake kinetics of Cu(II)*

Figure 6 shows a plot of concentration changes as a function of reaction time for the adsorption of Cu<sup>2+</sup>. The amount of Cu<sup>2+</sup> adsorbed increases rapidly, and, after 15 min, 85% of the initial copper added (5.0 × 10<sup>-7</sup> M) is adsorbed and equilibrium is achieved. The half-time calculated, assuming pseudo-first-order kinetics, is t<sub>1/2</sub> = 8 ± 2 min. Similar behavior has been found for the adsorption of Cu<sup>2+</sup> by metal

Table 3. Binding constant to the surface of chitin.

	(R <sub>T</sub> ) (mol g <sup>-1</sup> )	Log [K <sub>H</sub> <sup>2</sup> (ml mol <sup>-1</sup> )]	Reference
Chitin	6.86 · 10 <sup>-6</sup>	8.95 ± 0.01	This work
Chitin*	5.88 · 10 <sup>-6</sup>	8.98 ± 0.03	This work
Algae	4.80 · 10 <sup>-5</sup>	7.3	1

\*Same concentration of Cu<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> was added.  
1. XUE et al. (1988).

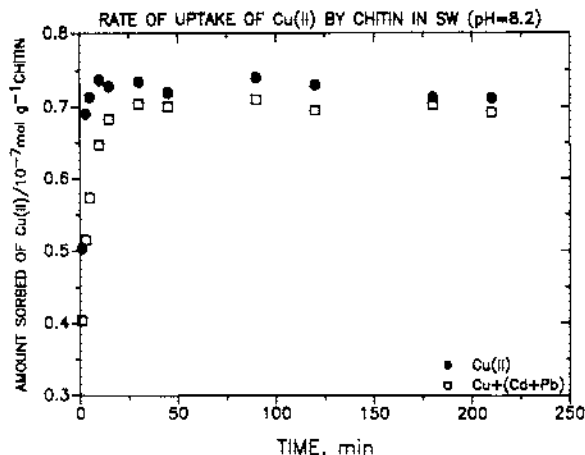


FIG. 6. The rate of adsorption of Cu(II) (1 μM) to chitin in seawater (pH = 8.2) in the absence and in the presence of Cd(II) and Pb(II) (0.5 μM).

oxide surfaces (BALISTRERI and MURRAY, 1982), phytoplankton (FISHER, 1985), algae (XUE et al., 1988; GONCALVES and LOPES DA CONCEICAO, 1989), and bacteria (GORDON and MILLERO, 1987).

*Effect of pH, temperature, and salinity in the adsorption of Cu<sup>2+</sup> to chitin*

Adsorption of Cu(II) (and other metal ions) at the solid chitin surface-water interface is strongly pH-dependent (Fig. 7), because the properties of both the chitin surface (charge and potential) and the solution composition (metal ion speciation) change with pH.

Using Eqn. (13), we obtain

$$\log \left\{ \frac{RCu}{[Cu^{2+}]} \right\} = Z + n \text{ pH} \quad (20)$$

where Z = log \*K<sub>H</sub><sup>2</sup> + n log {RH<sub>n</sub>}, and, if Z is considered to be constant,

$$\log \left\{ \frac{[Cu^{2+}]_{ads}}{[Cu^{2+}]_{sol}} \right\} = Z + n \text{ pH}. \quad (21)$$

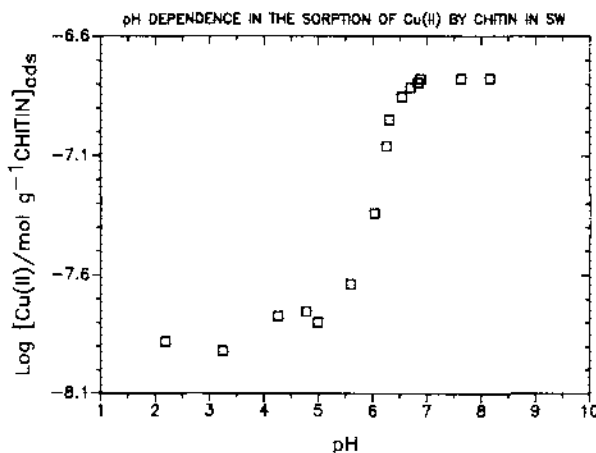


FIG. 7. Effect of pH on the adsorption of Cu(II) (1 μM) to chitin in seawater (S = 35‰) at 25°C.

According to Fig. 7, when a concentration of  $1 \mu\text{M}$  of  $\text{Cu}^{2+}$  is added to a chitin suspension in seawater, most of the copper will be adsorbed to the chitin surface groups. At a pH lower than 5.5, corresponding with the  $\text{pH}_{\text{PZC}}$  for the chitin surface groups, most of the copper remains in solution. Similar behavior of the effect of pH on the adsorption of  $\text{Cu}^{2+}$  has been shown for oxide and biological surfaces ranging from phytoplankton to algae and bacteria (BALISTRERI and MURRAY, 1982; GORDON and MILLERO, 1987; XUE et al., 1988).

Between pH 5.6 and 6.5 (Fig. 7), if  $Z$  is considered constant, the slope should be 2. In our case, the slope found is  $1.45 \pm 0.08$ , a lower value than expected. The cause of the difference may be that the values of  $Z$  are not constant even if the amount of Cu adsorbed is very small. The different sites on the chitin surface may change with pH. The low value may also due to the adsorption of anions, directly or indirectly as counterions. The formation of multinuclear hydroxo Cu(II) species may also occur (XUE et al., 1988; LAITINEN and ZHOU, 1988; FARLEY et al., 1985). Further studies are needed to elucidate the solution speciation effects on the adsorption of  $\text{Cu}^{2+}$  on chitin.

Temperature plays an important role in adsorption. There is no general rule for predicting the influence of the temperature on metal ion adsorption, and therefore one should expect variations in both directions. The adsorption of  $\text{Cu}^{2+}$  decreases at higher temperature. Similar behavior is found for the adsorption of gases on solids and phosphate on goethite (MACHESKY et al., 1989).

The specific adsorption energy  $E$  was calculated for the adsorption of copper on chitin using the equation

$$K_p = A \exp(-E/RT), \quad (22)$$

where  $A$  is the frequency factor, which is independent of temperature, and  $K_p$  is the partition coefficient of  $\text{Cu}^{2+}$  on chitin. The values of  $\ln K_p$  versus  $1/T$  (K) are shown in Fig. 8. The linear fit gives a value of  $E = -3.8 \pm 0.9 \text{ kcal mol}^{-1}$ . This negative specific adsorption energy of  $\text{Cu}^{2+}$  may be interpreted as the heat of hydration of Cu(II) being lower than its heat of adsorption.

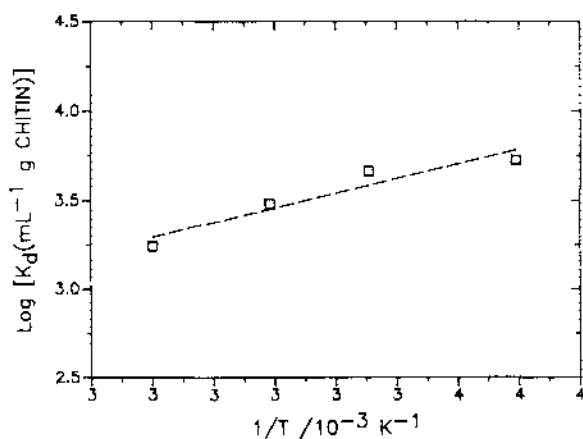


FIG. 8. Effect of temperature (K) on the adsorption of Cu(II) ( $1 \mu\text{M}$ ) on chitin in seawater ( $S = 35$  and  $\text{pH} = 8.1$ ).

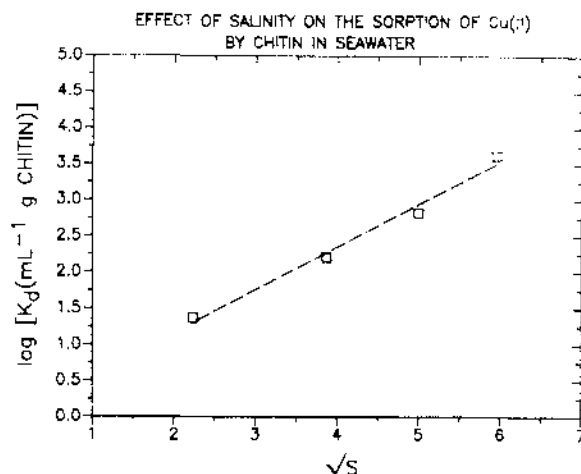


FIG. 9. Effect of salinity on the adsorption of Cu(II) ( $1 \mu\text{M}$ ) to chitin at  $25^\circ\text{C}$  and  $\text{pH} = 8.1$ .

The effect of salinity on metal ion adsorption on chitin has received little attention. Most of the studies on chitin have been carried out in natural and waste water. The studies in seawater (MUZZARELLI, 1973, 1977; MUZZARELLI and TANFANI, 1982) were made with chitosan due to its higher ability to adsorb metal ions. The salinity can influence adsorption by affecting the activities of the metal ions in solution, as well as affecting surface charge and double-layer capacitance of the hydrated particles. Increasing ionic strength usually increases the aggregation of suspended particles. Increased aggregation, in turn, is likely to increase the time-dependent partition of sorption, reflecting the necessity of solute diffusion into interaggregate pores. Concomitantly, both the exterior surface and the rapidly reversible component of sorption decrease. Thus, depending upon the reaction time used, sorption could appear to decrease. For this reason, overnight stabilization of the samples at four different salinities obtained for dilution of the seawater were carried out. The corresponding variation of the partition coefficient of  $\text{Cu}^{2+}$  to chitin at the different salinities is shown in Fig. 9. A linear relation between  $\log K_p$  and  $S^{1/2}$  gives a positive slope of 0.59, showing an increase in the amount adsorbed when the salinity increases. This may result in chitin being more important in transporting metals in seawater, where it is more abundant, than in fresh waters.

#### Competition with other metals

In the previous experiments only  $\text{Cu}^{2+}$  was added to the adsorbent to study the adsorption behavior. In natural aqueous systems, several metallic ions will be present and a selective uptake of these metals may be expected. In order to investigate its selectivity, a mixture containing  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cd}^{2+}$  was equilibrated with chitin.

Figure 6 shows the effect of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  on the adsorption of  $\text{Cu}^{2+}$  as a function of reaction time. Again, a rapid increase on the amount of Cu(II) adsorbed is observed. The half-time calculated, assuming a pseudo-first-order kinetic, is  $13 \pm 2$  min. Only a small increase in the half-time is observed, indicating that in the beginning the highest affinity surface ligands of chitin surface are rapidly occupied by the

stronger adsorbed Cu<sup>2+</sup>, and then a slight competition for these sites and for the lower affinity ones exist. After this increase, an equilibrium with the chitin surface is obtained, and almost the same amount (85%) of Cu<sup>2+</sup> added is adsorbed by the chitin surface groups.

Figure 4 shows the Cu<sup>2+</sup> Langmuir isotherm (Eqn. 13) when the same concentrations of Cu<sup>2+</sup>, Cd<sup>2+</sup>, and Pb<sup>2+</sup> are added to chitin. It can be observed that as a consequence of the competition for the highest affinity surface ligands, when a higher amount of each metal is added, a lower concentration of Cu<sup>2+</sup> is adsorbed. Using the transformed Langmuir equation (Eqn. 14) as it is shown in Fig. 5, a value of  $5.9 \times 10^{-6}$  mol g<sup>-1</sup> for the complexing capacity  $\{R_T\}$  and a value of  $9.0 \pm 0.1$  for log  $K_H^{\pm}$  are obtained (Table 3). A quantity of  $1.0 \times 10^{-6}$  mol g<sup>-1</sup> less Cu<sup>2+</sup> is adsorbed in this case, being replaced by Cd<sup>2+</sup> and Pb<sup>2+</sup>. Since no changes occur in the conditional constant, the sites occupied by copper are the same.

### Conclusions

The adsorption of Cu<sup>2+</sup> on chitin has been measured as a function of pH, temperature, and salinity. Its acid-base properties have been characterized in 0.7 M NaCl in terms of a two-protic acid-base system. The adsorption of Cu<sup>2+</sup> on chitin can be correlated with a surface complex formation equilibria or its mathematically equivalent Langmuir isotherm. Variations in factors such as pH, temperature, and salinity have additional (positive or negative) effects on the mobilization of copper. The presence of other transition metals does not affect the adsorption of Cu<sup>2+</sup> on chitin due to its higher affinity for the chitin surface groups.

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