Complexing Abilities of Hydrous Manganese Oxide Surfaces and their Role in the Speciation of Heavy Metals

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Manganese oxides play an important role in regulating heavy metals in aquatic systems. In order to understand their physico-chemical properties, hydrous manganese oxides were synthesized and interactions with heavy metals, especially Cu^{2+}, Pb^{2+}, Zn^{2+} and Cd^{2+} have been studied.

Complexing capacities as well as surface complexation constants at pH 5.5, 6.0 and 6.5 have been determined by differential pulse polarography (DPP). The DPP method enables one to do metal speciation measurements as it discriminates between free metal ion and complexed species.

Surface complexation constants were evaluated by linearizing the titration data using two different methods viz. Scatchard and van den Berg-Ružić plot methods. The results yielded by both methods are in good agreement.

Adsorption of heavy metals onto these oxides were also studied over a wide range of pH. Atomic absorption spectrometry was used for the analyses of these metals. The metal analyses were carried out in samples filtered through 0.2 μm filter. The drawback of this method is that filtrates are contaminated with fine oxide particles.

Plots of % metal adsorbed *vs.* pH showed sigmoidal curves. Plots of log $^cK_{SM}$ ($^cK_{SM}$ = conditional stability constant) obtained from adsorption data *vs.* pH yielded straight lines in the pH range of the adsorption edge. Thus this method can be applied for the prediction of metal speciation.

INTRODUCTION

In the past decade, metal speciation has received considerable attention owing to the fact that toxicity and biological uptake of metals has been shown to be dependent upon the metal form. In aquatic systems, speciation of metal ions may be governed by the presence, among others, of particulate organic matter (i.e. humic and fulvic acids), living organisms (algae and bacteria), inorganic hydrous oxides, hydroxydes, carbonates and clays.

In such systems for example, particulate MnO_x plays an important role in the metal speciation by adsorbing trace metal ions. The chemistry and biogeochemical cycle of manganese in natural waters is controlled to a large extent by chemical redox reactions between soluble Mn(II) and insoluble manganese oxides, MnO_x, especially at the redox boundary.[1]

Such hydrous oxide surfaces may be thought of as ligands and therefore the surface complexation can be treated in the same manner as equilibria in solution.[2]

In this paper, the determination of the binding constants between hydrous manganese oxide surface and some metal ions, i.e. Pb(II), Cu(II), Cd(II) and Zn(II) at various pH values and their respective complexing capacities have been reported.

EVALUATION OF THE DATA

At a constant pH and fixed ionic strength, the interaction between metal ions and surface binding sites of hydrous oxides may be described by the following reaction:

$$S + M \leftrightharpoons SM \tag{1}$$

where S represents uncomplexed surface sites and M the metal ion in solution (charges have been omitted for simplicity).

Because H^+ competes for binding sites and the buffer employed to keep the pH constant, i.e. 2-[N-morpholino] ethane sulfonic acid (MES) competes for the metal ions, conditional stability constants, $^cK_{SM}$, should be used to describe surface complexation.

$$^cK_{SM} = \frac{[SM]}{[S][M]'},\qquad(2)$$

where

$$[M]' = [M] + [MES-M]\qquad(3)$$

It must be emphasized that the electrical double-layer effects are implicitly incorporated in the conditional stability constant.

For comparison purposes, we have used two linearization methods for the determination of the conditional stability constants viz:

1) The method proposed by van den Berg,[3,4] Ružić[5,6] and Lee[7] which will be referred to as van den Berg-Ružić method. In principle, this method is suitable for the determination of the complexing capacity, i.e. total binding sites, $[S]_T$.
2) The Scatchard method.[8,9]

In the pH range of adsorption edge, the approach proposed by Laxen[10] has been applied for the determination of the conditional stability constant.

van den Berg-Ružić method

The mass balance for total metal, $[M]_T$ and total binding sites $[S]_T$, is given by:

$$[M]_T = [M]' + [SM]\qquad(4)$$

$$[S]_T = [S] + [SM].\qquad(5)$$

Under the pH conditions chosen for this study the M(II) hydroxo-complexes may be neglected.

$[M]'$ represents the electroactive form of metal ion and has been measured by differential pulse polarography (DPP). Combining Eqs

(2)–(5) and rearranging give the following expression:

$$\frac{[M]'}{[M]_T - [M]'} = \frac{1}{[S]_T \cdot {}^cK_{SM}} + \frac{1}{[S]_T} \cdot [M]' \tag{6}$$

Thus as plot of $[M]'/[M]_T - [M]'$ vs. $[M]'$ should yield a straight line with slope equal to $[S]_T^{-1}$ and intercept equal to $([S]_T \cdot {}^cK_{SM})^{-1}$ provided that only 1:1 complex is formed.

Scatchard method

This method requires a knowledge of the total binding sites. In the case of hydrous oxide surfaces, the total binding sites are related to the total concentration of surface hydroxyl groups, $[SOH]_T$, i.e. the maximum exchange capacity[11] is defined as:

$$[SOH]_T = [SOH_2^+] + [SOH] + [SO^-] \tag{7}$$

If there are n_i non equivalent class of binding sites per molecule of SOH, then the ith conditional stability constant for the complexation of M by the ith site is given by:

$${}^cK_{SM}^i = \frac{[SM]}{[M](n_i[SOH]_T - [SM]} \tag{8}$$

The extent of binding is expressed in terms of formation function, $\bar{V}$, defined as:

$$\bar{V} = \frac{\text{metal bound}}{\text{total binding sites}} = \frac{[SM]}{[SOH]_T} \tag{9}$$

Introducing $\bar{V}$ in Eq. (8) and rearranging yield the following expression (commonly known as Scatchard equation):

$$\frac{\bar{V}}{[M]'} = {}^cK_{SM}^i \cdot n_i - {}^cK_{SM}^i \cdot \bar{V} \tag{10}$$

In the case of 1:1 complex formation where only one class of binding sites $(i = 1)$ is involved, the plot of $\bar{V}/[M]'$ vs. $\bar{V}$ should give a straight line of slope equal to $-{}^cK_{SM}$.

Laxen method

Adsorption data are usually reported in terms of percentage adsorption:

$$\% \, ads = \frac{[SM]}{[SM]+[M]} \cdot 100. \tag{11}$$

Equation (11) can be readily transformed to obtain the ratio [SM]/[M]:

$$\frac{[SM]}{[M]} = \frac{\% \, ads}{(100-\% \, ads)}. \tag{12}$$

Therefore

$$^{c}K_{SM} = \frac{\% \, ads}{[S](100-\% \, ads)} \tag{13}$$

[S] is an experimental parameter which can be obtained from the total binding sites, i.e. the maximum exchange capacity, determined experimentally.

RESULTS AND DISCUSSION

In this study, the interactions of hydrous manganese oxide surface with some transition metal ions, i.e. Pb(II), Cu(II), Cd(II) and Zn(II) has been investigated. Residual labile metal ion concentrations have been measured, without any phase separation, by differential pulse polarography (DPP) in MES buffer (pH $\sim$ 5.5, 6.0 and 6.5). All measurements werre carried out at 25 °C in 0.1 M NaClO$_4$.

Typical titration curves for the interactions of MnO$_x$ surface with Pb(II) are shown in Figure 1. The shape of these voltammetric titration curves suggests that:

i) At low metal/ligand ratio, the slope is markedly reduced as compared to the calibration curve indicating the formation of strong and non-labile complexes.[12]

ii) At high metal/ligand ratio, the slope approaches that of the calibration curve suggesting that the maximum metal complexing capacity has been approximately attained.
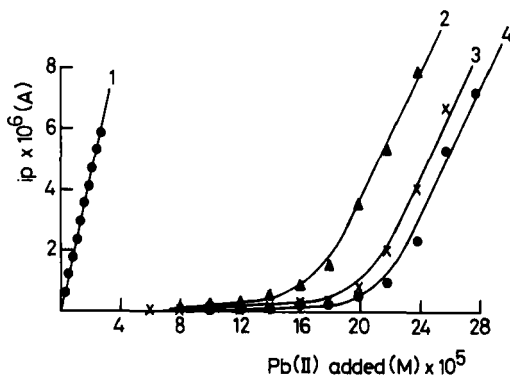
Figure 1 DPP-titration curves of hydrous manganese oxide surface with Pb^{2+} in MES buffer 0.02 M at $I = 0.1$ M $NaClO_4$ and $T = = 298$ K.
1. calibration curve;
2. $[MnO_x] = 0.0996\,g\,dm^{-3}$, $pH = 5.52 \pm 0.02$;
3. $[MnO_x] = 0.0994\,g\,dm^{-3}$, $pH = 5.97 \pm 0.03$;
4. $[MnO_x] = 0.1010\,g\,dm^{-3}$, $pH = 6.48 \pm 0.03$.

   iii)   With increasing pH, Pb(II) binds more strongly to MnO_x surface.

These trends have been observed for all of the metal ions investigated.

The binding parameters were evaluated by the van den Berg-Ružić[3-6] and Scatchard[8,9] plot methods (Figures 2 and 3). The results indicate:

   i)   1:1 complexes are indeed formed, otherwise a distortion would have been observed in the proposed plots.

   ii)   There is only one class of equivalent binding sites on hydrous manganese oxide surface as has been previously suggested by Gonçalves et al.[13].

   iii)   No kinetic effects can be observed, since the presence of such an effect will cause deviation from linearity in the van den Berg-Ružić and Scatchard plots.[6,14,15].

The conditional stability constants determined by the two methods together with the complexing capacity, $[S]_T$, evaluated by van den Berg-Ružić method, are given in Table 1. For comparison purposes, the maximum exchange capacity, $[SOH]_T$, has also been included.
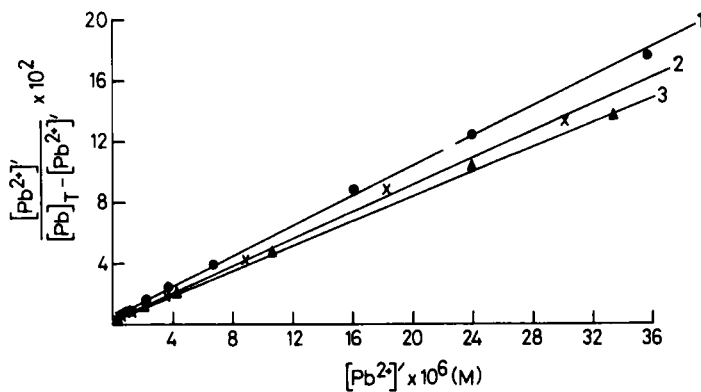
Figure 2 van den Berg-Ružić plots of the data taken from Figure 1.
1. $[MnO_x] = 0.0996\,g\,dm^{-3}$, pH $= 5.52 \pm 0.02$;
2. $[MnO_x] = 0.0994\,g\,dm^{-3}$, pH $= 5.97 \pm 0.03$;
3. $[MnO_x] = 0.1010\,g\,dm^{-3}$, pH $= 6.48 \pm 0.03$.
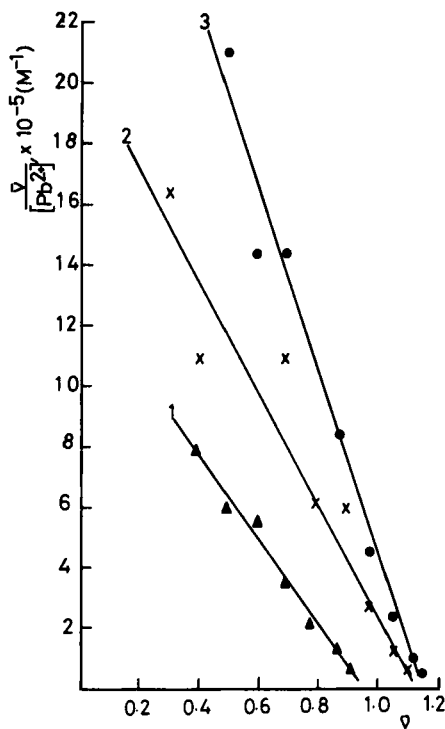
Figure 3 Scatchard plots of the data taken from Figure 1 (experimental conditions are the same as those given in Figure 2).

Table 1 Conditional stability constants, log $^cK_{SM}$, and complexing capacities, $[S]_T$, of $M(II)$-MnO_x ($T = 298$ K, $I = 0.1$ M $NaClO_4$, 0.02 M MES buffer)

M(II)	pH	Method				$\dfrac{[S]_T}{[SOH]_T} \times 100$
		van den Berg-Ružić		Scatchard		
		$[S]_T \times 10^4$	$log\,^cK_{SM}$	$log\,^cK_{SM}$	$[SOH]_T \times 10^4$	
Pb	5.52 ± 0.02	2.05 ± 0.03	5.94 ± 0.08	6.15 ± 0.03	2.04 ± 0.01	100
	5.97 ± 0.03	2.13 ± 0.02	6.40 ± 0.07	6.25 ± 0.05		104
	6.48 ± 0.03	2.36 ± 0.01	6.42 ± 0.02	6.49 ± 0.03		116
Cu	5.47 ± 0.03	2.39 ± 0.07	5.32 ± 0.07	5.36 ± 0.09	4.06	59
	5.96 ± 0.03	3.2 ± 0.1	5.54 ± 0.05	5.55 ± 0.06	4.08	78
	6.47 ± 0.01	3.0 ± 0.1	6.30 ± 0.07	6.29 ± 0.07	5.06	59
Cd	5.50 ± 0.02	0.62 ± 0.01	5.07 ± 0.07	5.07 ± 0.05	2.04 ± 0.01	30
	5.98 ± 0.02	0.93 ± 0.05	5.01 ± 0.15	5.00 ± 0.03		46
	6.53 ± 0.01	0.93 ± 0.02	5.05 ± 0.08	4.96 ± 0.03		46
Zn	5.97 ± 0.01	0.47 ± 0.02	4.50 ± 0.07	4.52 ± 0.03		23
	6.48 ± 0.01	1.15 ± 0.05	4.88 ± 0.09	4.75 ± 0.06		56

Despite the fact that experimental points are more widely scattered in Scatchard plot method[15] than in van den Berg-Ružić plot method (Figures 2 and 3), log $^cK_{SM}$ values obtained by both methods are in good agreement within experimental errors. The conditional stability constants increase with an increase in pH (Table I) and stability constants increase in the order: $Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+}$. The same order has been found for other hydrous oxide such as SiO_2(am), $\gamma - Al_2O_3$ and TiO_2.[16] The same trend is observed for the complexing capacity and its dependence on the interacting metal ion is highlighted by $[SOH]_T/[S]_T$ ratio. Except for lead, the complexing capacity is systematically less than the total of binding sites, i.e. the maximum exchange capacity. The drawback of van den Berg-Ružić method in the evaluation of total binding sites is reflected in the Scatchard method by the average number of binding sites, n, per molecule of complexant. For Pb^{2+}, $1.0 \leq n \leq 1.16$ whereas $0.23 \leq n \leq 0.78$ for other metal ions investigated. In the case of Pb^{2+}, n is approximately unity, indicative of 1:1 complexation while for those metal ions where n is approximately 0.5, one may infer that 1:2 complexes are formed.[17] However, the linearity of both Scatchard and van den Berg-Ružić plots are indicative of 1:1 complex, which is contradictory to the observed results for the values of n. As

Klotz pointed out,[18] care should be taken while interpreting n values from Scatchard plots.

Plots of $\log {}^cK_{SM}$ obtained from adsorption data via Eq. (13) *vs.* pH are presented in Figure 4. In the pH range of adsorption edge, these plots result in straight lines. For hydrous manganese oxide investigated, the adsorption edge lies in the acidic region (pH < 5), especially in the case of Pb^{2+}, adsorption of 98.9–100% was found in the pH range 1.0–2.5. This observation would be expected since
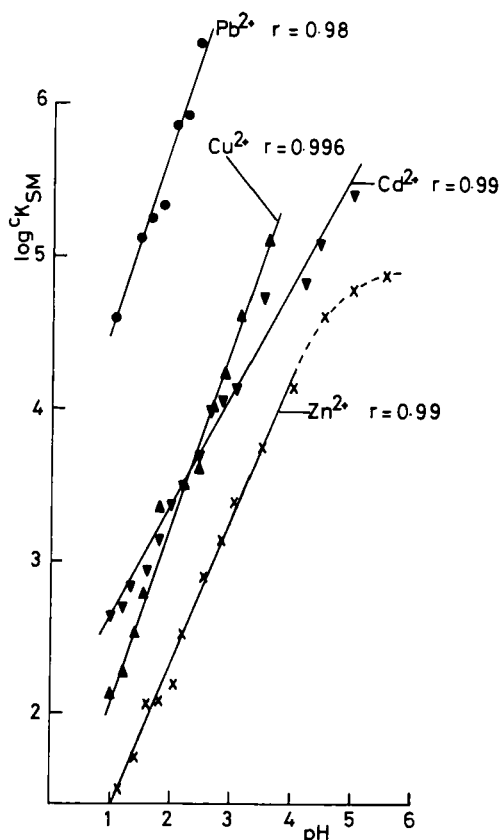
Figure 4 $\log {}^cK_{SM}$ as a function of pH in the range of adsorption edge; $[MnO_x] = 0.995 \pm 0.008\ g\,dm^{-3}$
pH: adjusted by dropwise addition of $HClO_4$ or NaOH
$I = 0.1\ M\ NaClO_4$, $T = 298\ K$.

the pH_{zpc} of MnO_x investigated is 2.47 ± 0.04.[18] The slope obtained from linear regression analysis for Pb^{2+}, Cu^{2+}, Cd^{2+} and Zn^{2+} were found to be 1.2, 1.2, 0.72 and 0.94 respectively. The slope values, approximately equal to unity are indicative of 1:1 complexation reaction, i.e. one proton released per metal ion adsorbed. Beyond the pH range of adsorption edge, one would expect the plots to level off or at least a decrease in the slopes should be observed.[19]

The results of this study have shown that hydrous manganese oxides are strong complexants for trace metal ions and hence, play an important role in the speciation of trace metals in natural systems.

CONCLUSIONS

The conditional stability constants $(5.5 \leq pH \leq 6.5)$ determined by van den Berg-Ružić and Scatchard plot methods were found to be in good agreement. However, the complexing capacity determined by the van den Berg-Ružić method as well as the average number of binding sites, n, determined by the Scatchard method are not representative of the total number of binding sites. The maximum exchange capacity method is more suitable than the above methods for the evaluation of total number of binding sites.

It must be emphasized that the concept of "complexing capacity" is conditional since it is dependent on several parameters such as pH, ionic strength, nature of metal ion, metal/ligand ratio...

The Laxen approach seems to be promising for metal ion speciation in the pH range of adsorption edge, in particular for hydrous oxides whose pH_{zpc} lies in the pH range of natural waters.

The conditional stability constants for the complexation of metal ions investigated with MnO_x suggest that hydrous manganese oxide is one of the complexing agents of natural waters that governs the transport and bioavailability of heavy metal ions in natural aquatic systems.

References

1. W. Davison. In: *Chemical Processes in Lakes* (W. Stumm, ed.) (Wiley-Interscience, 1985), 31.
2. P. W. Schindler and W. Stumm. In: *Aquatic Surface Chemistry, Chemical Processes at Particulate-Water Interface* (W. Stumm, ed.) (Wiley-Interscience, 1987), 83.

3. C. M. C. van den Berg and J. R. Kramer, *Anal. Chim. Acta* **106**, 113 (1979).
4. C. M. C. van den Berg, *Mar. Chem.* **11**, 307 (1982).
5. I. Ružić, *Anal. Chim. Acta* **140**, 99 (1982).
6. I. Ružić. In: *Complexation of Trace Metals in Natural Waters* (C. J. Kramer and J. C. Duinker, eds.) (Nijhoff and Junk. Publ., The Hague, 1984), 31.
7. J. Lee, *Wat. Res.* **17**, 501 (1983).
8. G. Scatchard, *Ann. N.Y. Acad. Sci.* **51**, 660 (1949).
9. G. Scatchard, J. S. Coleman and A. L. Schen, *J. Am. Chem. Soc.* **79**, 12 (1957).
10. D. P. H. Laxen, *Sci. Tot. Environ.* **30**, 129 (1983).
11. P. W. Schindler, B. Fürst, R. Dick and P.V. Wolf, *J. Colloid Interface Sci.* **55**, 469 (1976).
12. H. P. van Leeuwen, *Sci. Tot. Environ.* **60**, 45 (1987).
13. M. L. Gonçalves, L. Sigg, M. Reutlinger and W. Stumm, *Sci. Tot. Environ.* **60**, 105 (1987).
14. I. Ružić and S. Nikolic, *Anal. Chim. Acta* **140**, 47 (1982).
15. C. J. M. Kramer, *Mar. Chem.* **18**, 335 (1986).
16. P. W. Schindler. In: *Metal Ions in Biological Systems*, vol. 18 (H. Sigel, ed.) (Marcel Dekker Inc., N.Y., 1984) 106.
17. A. Castetbon, M. Corrales, M. Astruc, M. Dotin, R. M. Serritt and J. N. Lester, *Environ. Technol. Lett.* **7**, 495 (1986).
18. A. Balikungeri and W. Haerdi, *Int. J. Environ. Anal. Chem.* **23**, 239 (1986).
19. R. J. Davis-Collex, P. O. Nelson and K. J. Williamson, *Environ. Sci. Technol.* **18**, 491 (1984).