Metal Ion Adsorption to Complexes of Humic Acid and Metal Oxides: Deviations from the Additivity Rule

5 AUTHORS, INCLUDING:

Arnoldus Wilhelmus petrus Vermeer

Bayer CropScience

26 PUBLICATIONS   **1,237** CITATIONS

Luuk K Koopal

Wageningen University

291 PUBLICATIONS   **8,846** CITATIONS

Metal Ion Adsorption to Complexes of Humic Acid and Metal Oxides: Deviations from the Additivity Rule

ARNOLDUS W. P. VERMEER,*,†,‡
JENNY K. MCCULLOCH,†
WILLEM H. VAN RIEMSDIJK,§ AND
LUUK K. KOOPAL†

*Laboratory of Physical Chemistry & Colloid Science,
Wageningen Agricultural University, Wageningen,
P.O. Box 8038, 6700 EK Wageningen, The Netherlands, and
Department of Soil Science & Plant Nutrition,
Wageningen Agricultural University, Wageningen,
P.O. Box 8005, 6700 EC Wageningen, The Netherlands*

The adsorption of cadmium ions to a mixture of Aldrich humic acid and hematite is investigated. The actual adsorption to the humic acid−hematite complex is compared with the sum of the cadmium ion adsorptivities to each of the isolated components. It is shown that the sum of the cadmium ion adsorptivities is not equal to the adsorption to the complex. In general, the adsorption of a specific metal ion to the complex can be understood and qualitatively predicted using the adsorptivities to each of the pure components and taking into account the effect of the pH on the interaction between humic acid and iron oxide on the metal ion adsorption. Due to the interaction between the negatively charged humic acid and the positively charged iron oxide, the adsorption of metal ions on the mineral oxide in the complex will increase as compared to that on the isolated oxide, whereas the adsorption to the humic acid will decrease as compared to that on the isolated humic acid. As a result, the overall adsorption of a specific metal ion to the complex will be smaller than predicted by the additivity rule when this metal ion has a more pronounced affinity for the humic acid than for the mineral oxide, whereas it will be larger than predicted by the additivity rule when the metal ion has a higher affinity for the oxide than for the humic acid.

Introduction

The speciation of heavy metal ions has been studied in natural soil systems (*1*, *2*) as well as in model systems (*3*, *4*). Knowledge of the binding of the metal species to soil systems is of importance for the prediction of the movement of these species and for the way in which they are distributed in the environment. McLaren et al. (*2*) and Bibak (*5*) have found that metal ion adsorption characteristics of complete soils are controlled to a large extent by their organic matter and metal oxide content.

To explain the overall binding, Bibak (*5*) has compared the adsorption of different metal ions to an entire soil with their adsorption to the single components in this soil system. The calculated adsorptivities, assuming additivity, were only about half the measured values for the entire soil. Although Bibak concludes that the additivity can only be applied under restricted conditions, an alternative procedure is not given.

Several authors have simplified the situation by studying the binding of metal ions to well-defined model systems. For instance, the adsorption of metal ions to humic substances (*6*−*12*) and to iron oxides (*14*−*22*), two important components of many types of soils, has been investigated in detail. Robertson (*4*, *23*) measured copper binding to a goethite−humic acid mixture and reported a significantly lower adsorption than the simple sum of the adsorptivities of the noninteracting components, similar to what Bibak found for the entire soil. On the other hand, there are also studies that indicate that the adsorption of metal ions onto metal oxide−humic acid mixtures is increased due to the interactions between these two components (*1*, *3*, *4*, *24*−*28*). However, these studies mainly compared the metal binding to the mixture with that to the bare oxide only, neglecting the binding to the pure humic. It is clear that, even for simple mineral oxide−humic acid complexes, the additivity of adsorptivities does not apply under all circumstances and that metal ion binding to these complexes is not yet fully understood.

Vermeer et al. (*12*, *29*) have studied the overall proton adsorption to a complex of humic acid and hematite. It has been shown that the proton adsorption is clearly affected by the interaction between humic acid and hematite. At low pH, a decreased proton adsorption is observed as compared to the sum of the adsorptivities due to a loss of binding sites for the protons on the humic acid. At relatively high pH, an increased proton adsorptivity occurs at the metal oxide due to the fact that the adsorbed humic acid screens the positive electric field of the metal oxide very effectively.

It seems most probably that the adsorption of metal ions will be affected in a similar way. The aim of the present work is therefore to determine at different pH values the binding of heavy metal ions and cadmium ions in particular to iron oxide and humic acid individually and to the complex of these components. To analyze the observations, the sum of the adsorptivities to the individual components will be calculated (the additivity rule), and the result will be compared with the measured adsorption to the complex. Deviations from the additivity rule will be discussed in view of what is known about the effect that the adsorption of humic acid onto the oxide has on the proton adsorptivity. To enable the comparison with the binding to the individual components, we will start with a short description of the metal ion adsorption in the isolated systems (humic acid or hematite) as a function of pH and then consider the adsorption characteristics of cadmium to the complex (humic acid adsorbed to hematite). After the discussion of the cadmium results, literature data on copper adsorption and the differences in adsorption behavior between cadmium and copper will be discussed.

Experimental Procedures

All experiments have been performed in a thermostated room at 21 ± 1 °C, and the water is purified by percolating it through a mixed-bed ion exchange column and a commercial water purification unit (Elgastat UHP-3 (Elga)). Other chemicals (cadmium nitrate, potassium nitrate, hydrochloric acid, and potassium hydroxide) were obtained from Fluka (p.a. quality) and are used without further purification.

* Corresponding author phone: (49) 214 3023988; fax: (49) 214 3050698; e-mail: Ronald.Vermeer.RV@Bayer-AG.de.
† Laboratory of Physical Chemistry & Colloid Science.
‡ Present address: Bayer AG, ZF Biophysik, Building E 41, D-51368 Leverkusen, Germany.
§ Department of Soil Science & Plant Nutrition.

	pH 4	pH 6	pH 9
PAHA (C g^{-1})	−106	−252	−384
hematite (mC m^{-2})	157	80	−5

[a] Data are obtained from ref 30.

Humic Acid. Aldrich humic acid was purified from insoluble material and brought in its proton form as described in ref 30. The purified sample, denoted as PAHA, was freeze-dried and stored in a glass container. The concentration of trace metals in PAHA was below the detection limit of ICP measurements (Spectro flame ICP−OES). Before use PAHA was resuspended overnight in a KOH solution with pH approximately 10 to a concentration of 2 g L^{-1} to fully disperse the sample. Other PAHA solutions were made from this stock solution. The charge density of isolated PAHA was measured by potentiometric proton titrations (30), and the charge densities at pH 4, 6, and 9 in 0.01 M KNO_3 are summarized in Table 1.

Hematite. A well-aged hematite (α-Fe_2O_3) sample, prepared as described by Breeuwsma and Lyklema (31), was washed with HCl and dialyzed extensively against demineralized water. The particles have a mean size of 50 nm. The BET (N_2) surface area, measured with a NOVA 1000 Quantachrome, is 43 $m^2 g^{-1}$, and no significant porosity is observed. The surface charge density and the point of zero charge (pzc) were obtained from potentiometric proton titrations (30). The pzc of the hematite is 8.9, and the charge densities at pH 4, 6, and 9 in 0.01 M KNO_3 are given in Table 1.

Potentiometry and Flame AAS. Potentiometric measurements were made with the Wallingford titration system (32, 33). Cadmium ion concentrations were measured using an Orion 94-48 solid state sulfide-based cadmium ion-specific electrode (ISE), and the pH measurements were made with an Ingold U272-S7 glass electrode. In both cases, an Ingold 363-S7 Ag/AgCl reference electrode was used. The cadmium concentration and the pH were simultaneously measured while the solution was stirred continuously. A maximum time interval of 20 min was set for two successive additions of titrant. The total duration of the titrations was limited to 8 h or less. The cadmium ISE was calibrated (10) at the same salt concentration and pH at which the measurements were made. The calibration curves were found to be linear within the concentration range studied.

Flame AAS measurements were done using an S-11 atomic absorption spectrophotometer (Instrumentation Laboratory, Andover, MA). Before measurement, all samples were acidified to pH 1 by the addition of 0.25 mL of concentrated HNO_3. This prevents cadmium adsorption to the walls of the tubes, releases cadmium bound to the humic acid, and precipitates the humic acid present in the solution. The samples were corrected for background iron concentrations following Van der Lee et al. (34).

Cadmium Adsorption Measurements. The cadmium adsorption to the humic acid was measured potentiometrically. The amount of humic acid in the cell was 15 mg in 30 mL in 0.01 M KNO_3. Subsequent additions of a $Cd(NO_3)_2$ stock solution to the humic acid, equilibrated at the wanted pH and salt concentration, were made with a 1-mL Dosimat buret. Shifts of the pH after the addition of cadmium were corrected by adding 0.1 M HNO_3 or 0.1 M KOH from 5-mL burets connected to the titration system. The amount of humic acid in the cell was 15 mg in 30 mL in 0.01 M KNO_3.

Adsorption of cadmium to hematite and to the mixed systems was measured in batch experiments. The experiments were carried out in polyallomer centrifuge tubes of 50 mL that were cleaned with acid (37% HCl), washed with

purified water, and steamed. In all cases 2.5 mg of a 3.465 wt % suspension of hematite (3.7 m^2) was added to the tubes.

For the study of cadmium adsorption to pure hematite, water, salt, and acid or base were added to bring the solution with 3.7 m^2 hematite to the desired salt concentration (0.01 M) and pH. The final volume was 40 mL. A cadmium stock solution was then added from a 1-mL Dosimat buret, the pH was adjusted, and the suspensions were equilibrated for 4 h. At pH 4 and pH 6, the pH remained stable; at pH 9, where the Cd adsorption is relatively high, the pH of each of the tubes had to be readjusted to pH 9 and a further hour of equilibration was allowed. The tubes were centrifuged at 7500 rpm for 1 h using a Beckman JA-20 centrifuge (6800*g*). Approximately 5 mL of supernatant was taken from each tube and transferred to a clean dry polyallomer tube for the measurement of the total cadmium amount by flame AAS.

For the PAHA−hematite mixtures, purified water and PAHA (7 mL of a 0.5 g L^{-1} solution) were added with volumetric pipets to the 3.7 m^2 hematite suspension, and the salt concentration and pH were adjusted to the desired value. The PAHA adsorption was equilibrated overnight by head-over-head rotation. Then the cadmium solution was added from a 1-mL buret, and the system was equilibrated for 3 h. Then the pH was measured and restored to its original value, and an additional hour of equilibration was allowed. After centrifugation, the total cadmium concentration in the supernatant was determined by AAS as described above. The PAHA concentration in the supernatant was determined by UV absorption at 254 nm (Hitachi U3210 spectrophotometer). The total cadmium in the supernatant was divided into free Cd and Cd bound to PAHA in the supernatant by calculating first the amount of Cd bound to free PAHA by using the known Cd binding isotherm to PAHA at the given pH and salt concentration. The obtained amount was subtracted from the total Cd amount in the supernatant to obtain the free cadmium amount, and from this and the total volume (40 mL) the free Cd concentration was calculated. The remainder of the supernatant (approximately 30 mL) was used to determine the free cadmium concentration experimentally with the cadmium ISE. Both the calculated and measured free cadmium concentrations are used for the calculation of the cadmium adsorption to the complex.

Results and Discussion

Cadmium Adsorption to Humic Acid and Hematite. The cadmium adsorption to PAHA is plotted on a log−log scale in Figure 1 for three pH values. The cadmium adsorption to the humic acid increases with increasing pH. This is due to the fact that the negative charge of PAHA increases with increasing pH (30), see Table 1. Due to the electric field, the cadmium concentration in the solution near the PAHA binding sites is increased with respect to the bulk concentration, and this promotes the complexation.

The pH dependence of the metal ion adsorption is related to the number of protons that are released per metal ion bound. According to the Gibbs equation, the proton to metal ion ratio can be estimated from the graphs by taking the shift of the pCd at constant amount of metal bound per unit of sorbent divided by the pH difference between the curves (35, 36). For humic acid, the proton/cadmium exchange ratio varies somewhat with the cadmium loading. The average exchange ratio measured at around 0.06 mmol of cadmium/g of PAHA in the pH range of 4−9 is 0.7 (see Figure 1). This value is very similar to what has been measured before in case of cadmium binding to purified peat humic acid (PPHA) (37, 38). The slope of the log−log plots in Figure 1 varies somewhat with the cadmium loading and is maximal at low loading and low pH. For PAHA the highest slope is around 0.9, indicating nonideal behavior even at low cadmium
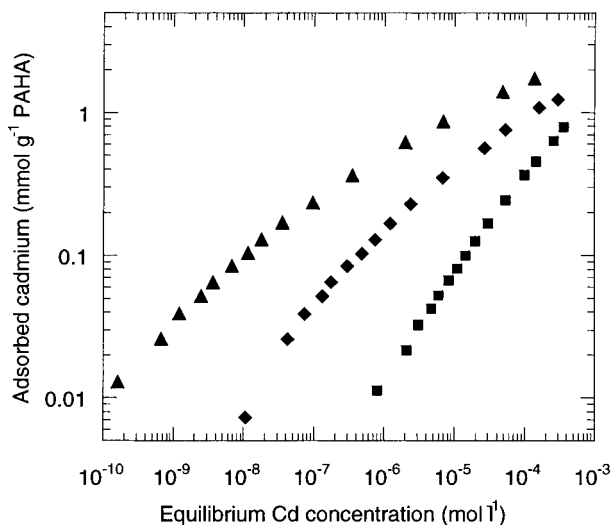
FIGURE 1. Cadmium binding to PAHA as a function of the equilibrium cadmium concentration for three different pH values and 0.01 M KNO₃: (■) pH 4; (◆) pH 6; (▲) pH 9.
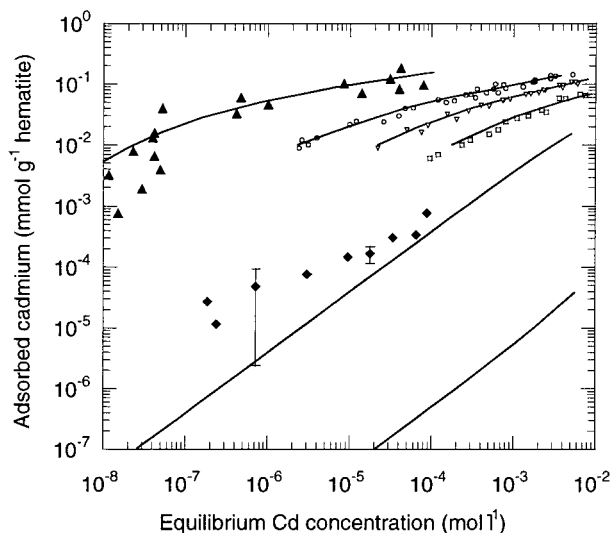

FIGURE 2. Cadmium binding to hematite as a function of the equilibrium cadmium concentration. Experimental results at 0.01 M KNO₃ obtained in this study: (◆) pH 6, (▲) pH 9; literature results (*19, 20*) in 0.02 M KNO₃: (○) pH 8.1, (▽) pH 7.56, (□) pH 6.94. Also added are cadmium adsorption isotherms calculated with ECOSAT (*40*) using the one-pK BS model (*39*) at the pH values and salt concentrations used in the experiments and at pH 4 and 0.01 M KNO₃. The model parameters were $pK_H = 8.9$, $N_s = 8$ sites nm⁻², $C_1 = 1.72$ F m⁻²; $pK^*_{CdOH} = 11.5$, see the text for further explanation.

concentration. Again this result for PAHA is very similar to that for cadmium binding to PPHA.

For hematite cadmium adsorption, data over a large concentration range and large pH range are difficult to obtain because of difficulties with the determination of the cadmium concentration in the presence of hematite. The experimental data set presented in Figure 2 is composed of newly measured data at pH 6 and pH 9 and literature data of Fokkink et al. (*19, 20*) at pH values of 6.94, 7.56, and 8.1. At pH 9, the cadmium concentrations were kept sufficiently low to prevent Cd(OH)₂ precipitation. The cadmium adsorption at pH 6 is about 2 orders of magnitude smaller than that at pH values around the pzc. At pH values below the pzc, the adsorption of cadmium ions to the hematite occurs against the electrostatic repulsion between the positively charged cadmium ions and the positive hematite surface. Therefore, the cadmium adsorption decreases with decreasing pH. More-

over, the adsorption at pH values below the pzc must be due to specific (nonCoulombic) interactions.

The average proton/cadmium exchange ratio that can be derived from the experimental results at a loading of 0.01 mmol g⁻¹ for the pH range of 7–9 is about 1.7. A proton exchange ratio higher than 1 but lower than 2 is commonly observed for cadmium binding to iron oxides (*21*). The slope of the cadmium binding curves also varies somewhat with metal ion loading. At low loading and low pH, a slope that approaches unity is expected if it is assumed that the isotherm follows the Henry adsorption law at very low concentration.

The cadmium ion binding to hematite with its proton/metal ion exchange ratio of about 1.7 is more strongly dependent on pH than the binding to humic acid with its proton/metal ion exchange ratio of about 0.7. Correspondingly, a much stronger variation of the cadmium ion binding with pH at constant metal ion activity is observed for hematite than for humic acid.

For a comparison of the present results with the experimentally measured cadmium adsorption to a PAHA/hematite complex, model calculations were applied to estimate the cadmium adsorption to hematite under the appropriate conditions. For the calculations, the simple one-pK BS (basic Stern) model has been applied to the cadmium–hematite system using the previously observed parameter values [Stern layer capacitance, $C_1 = 1.72$ F m⁻²; total site density, $N_s = 8$ sites nm⁻² (*39*)]. In this simple model, the charge of a site reverses from +0.5 to −0.5 upon release of a proton, and the logarithm of the proton adsorption constant equals pH$_{pzc}$. The pzc value is adjusted to 8.9, as observed in the present study and by Fokkink (*19*). The cadmium adsorption constant is adjusted accordingly to $pK^*_{CdOH} = 11.5$ (Cd is assumed to be adsorbed as CdOH). The curves shown in Figure 2 are calculated using the computer program ECOSAT (*40*). Although the model may simplify the actual situation, the predictions are sufficiently adequate for the present purpose.

The calculated adsorption isotherms are in good agreement with the experimental data points for pH values of 6.94, 7.56, 8.1, and 9. However, at pH 6 the experimental adsorptivities are higher than the calculated values. This is most likely due to experimental artifacts. The relatively high adsorption at pH 6 is probably due to the loss of cadmium by adsorption to the glassware (electrodes and pipets), which is included in the present data as adsorption to hematite. An estimate of the correction for this adsorption, based on an adsorption of 4.5×10^{-5} mmol cadmium onto the glassware at the present pH, is indicated for two points of the isotherm by the error bars in Figure 2. A similar reasoning results at pH 9 in error bars that are smaller than the experimental error.

The model predictions at pH 6 will be used as best estimates for the cadmium adsorption. At pH 4, it is not possible to make reliable measurements, and only the model calculations are available.

Cadmium Adsorption to Humic Acid–Hematite Complexes. Cadmium adsorption to the complex of PAHA and hematite was measured as a function of the cadmium concentration and pH for a system that had a constant amount of hematite and PAHA but a varying amount of cadmium. To judge the cadmium adsorption to the complex, it is relevant to specify the PAHA adsorption to hematite first. At all pH values a measurable amount of PAHA was left in solution. The adsorbed amounts and equilibrium concentrations of PAHA at the given pH values and salt concentration are summarized in Table 2. In two previous papers (*30, 41*), the adsorption of PAHA onto hematite has been discussed extensively using a polyelectrolyte adsorption model. In another study, Avena and Koopal (*42*) have discussed the sorption kinetics of PAHA on iron oxide and the reversibility of the adsorption. Most relevant for the

TABLE 2. PAHA Adsorption on Hematite at 0.01 M KNO₃ for Different pH Values at the Final Solution Concentrations of PAHA Indicated[a]

	pH 4	pH 6	pH 9
adsorbed amount (mg m^{-2})	1.0	0.8	0.55
final concentration (mg L^{-1})	8	26	50

[a] The conditions are the same as those in the Cd ion binding studies to the PAHA−hematite complex.
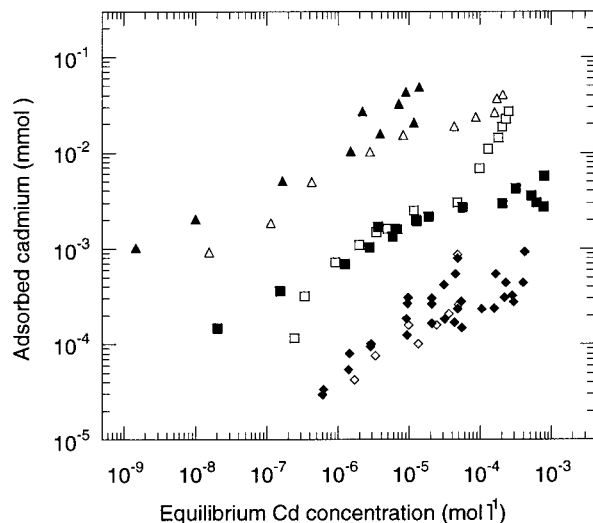

FIGURE 3. Cadmium adsorption to the PAHA−hematite complex at 0.01 M KNO₃ and three pH values. The solid and the open symbols refer to two different ways of calculation of the adsorption, see the text. In all cases the system contained 87 mg of hematite (corresponding with 3.7 m²), 3.5 mg of PAHA, and the total solution volume was about 40 mL. (◆/◇) pH 4; (■/□) pH 6; (▲/△) pH 9. The adsorbed amounts and concentrations of free PAHA at the given solution conditions are presented in Table 2.

present study is that the adsorbed humic acid molecules form a layer with both humic acid segments in direct contact with the hematite particles to accomplish charge compensation of the surface and with segments protruding into the solution. Furthermore, it was found that the humic acid molecules adsorb reversibly. At the cadmium concentrations studied, PAHA adsorption to hematite is not significantly affected by the presence of cadmium at pH 4 and pH 6. At pH 9, PAHA adsorption in the presence of cadmium is slightly higher than in the absence (30).

The amount of cadmium bound to the complex is shown in Figure 3 as a function of the free cadmium concentration. The cadmium binding is calculated in two ways that both depend on the measured binding isotherm of Cd to "free" PAHA. In the first method, the total amount of Cd in the supernatant (AAS) is subtracted from the total amount of Cd initially present, and the difference is plotted (closed symbols in Figure 3) versus the calculated concentration of free Cd in the supernatant (using the Cd−PAHA adsorption isotherm and the AAS result). In the second method, the free Cd concentration in the supernatant as measured with the ISE is used. The adsorption is now calculated as total cadmium minus the free amount in the solution and that bound to the "free" PAHA. The results are indicated by the open symbols. The latter method is probably less accurate because ISE measurements in solutions that have been in contact with hematite are not completely reliable. It follows from Figure 3 that (i) there is a considerable scatter in the results and (ii) some systematic differences exist between the two calculation methods. The uncertainty in the ISE measurements and the various steps in the calculations may explain these differ-

ences. For the moment, the results are acceptable and sufficient to test the additivity rule.

Some special attention is required for the results at pH 9. In principle, it is possible that at this pH Cd(OH)₂ precipitation occurs at high total cadmium concentrations. On the basis of the speciation diagram of cadmium in 0.01 M KNO₃, we may expect that, up to adsorption values of 2 × 10^{-2} mmol of Cd²⁺ to the complex, the Cd(OH)₂ precipitation can be neglected. The adsorption values larger than 2 × 10^{-2} mmol of Cd might be somewhat overestimated due to the fact that Cd(OH)₂ precipitation is "seen" as adsorption.

The measured Cd binding to the complex can be compared with the cadmium binding to the same amounts of isolated hematite and isolated humic acid and with the sum of these adsorptions. The additivity rule neglects any effect of the interaction between the bound humic and the hematite on the cadmium binding. For a clear comparison, the experimental results at the three pH values studied are replotted in Figure 4 (no distinction is made between the two calculation methods) together with the Cd binding to hematite (model predictions as shown in Figure 2), to PAHA, and to the Cd binding according to the additivity rule. The additivity rule neglects any effect of the interaction between the bound humic and the hematite on the cadmium binding. For the given conditions (amount of hematite, amount of PAHA, solution volume, and salt concentration), the adsorption to hematite at pH 4 and pH 6 is so small that it can be neglected relative to the amount of cadmium bound to the humic acid. At pH 9, the situation is different; at this pH the cadmium adsorption to hematite is dominant. Even when a large error would occur in the adsorption values of Figure 2, this conclusion remains valid.

Comparison of the measured results and the results calculated with the additivity rule shows that at pH 4 the measured binding is equal to or lower than the amount based on the additivity rule. At pH 6 and pCd < 4, the measured binding is somewhat above (note the log scale) what is expected on the basis of the additivity rule. At both pH values the sum is strongly dominated by the humic acid. At pH 9, the measured binding is approximately double the amount calculated with the additivity rule. The cadmium binding to hematite dominates the calculated sum of adsorptions, but the humic acid contribution is still visible. Apparently the cadmium binding to the complex cannot be described by the simple additivity rule.

To obtain more insight in the adjustment processes that occur upon adsorption of a polyelectrolyte to a charged surface, Vermeer et al. (30, 43) have made some model calculations. These calculations show that the potential at a variably charged oxide surface with a high pzc can decrease up to 60 mV due to the adsorption of a weak acidic polyelectrolyte. The magnitude of the change depends on the pH and on the amount of polyelectrolyte adsorbed. The calculations also show that the potential shift is maximal at intermediate pH values (43).

In general, a decrease of the positive surface potential by 30−60 mV corresponds with an increase of the pH in the bulk solution with about 0.5−1 unit. Such a shift may thus lead to cadmium adsorption values to the complex that are comparable to those on bare hematite at a solution pH value that is 0.5−1 unit higher than the actual value. Alternatively, one could reason that a decrease of 30−60 mV of the surface potential leads to an increase in the metal ion concentration in the layer adjacent to the surface, and this increase corresponds with a decrease in the pM of 1−2 units. Hence, at a given pH, the presence of adsorbed humic acid may have a similar effect on the cadmium adsorption than a pCd decrease by 1−2 units. At the hematite surface, some sites will also become unavailable for metal ion binding due to the binding of the humic, but the fraction of sites not in
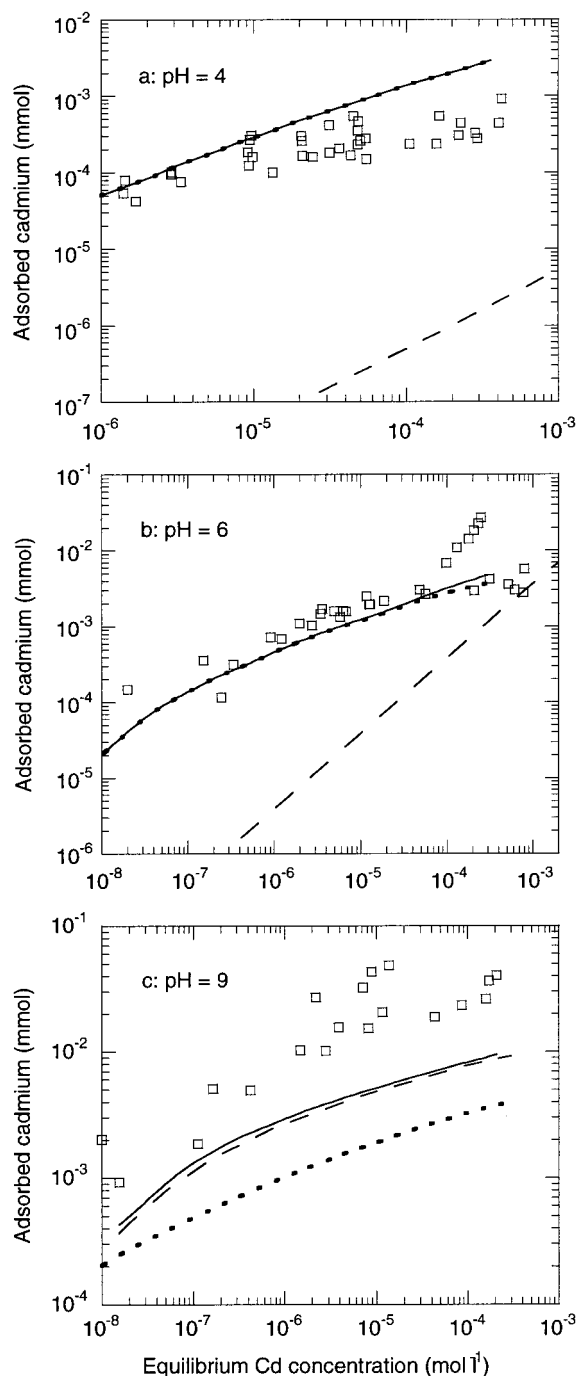
FIGURE 4. Comparison of the cadmium adsorption isotherms (symbols) onto the PAHA—hematite complex at 0.01 M KNO$_3$ and three different pH values: a, pH 4; b, pH 6; c, pH 9 with the single-component adsorptions and the adsorption according to the additivity rule. The adsorption isotherms to hematite are indicated by the dashed curves; those to PAHA are indicated by the dotted curves; and the noninteracting sum of the single-component adsorptions is shown by the solid curve. For experimental conditions, see Figure 3.

contact with a polyelectrolyte segment is still considerable due to the very high total site density of hematite. The overall effect is that the adsorptivity of the metal ions to hematite with adsorbed humic acid will increase as compared with that on bare hematite.

For the polyelectrolyte (humic acid), the positive or less negative potential near the acidic groups will lead to a lower affinity of the acid groups for metal ion binding than with "free" polyelectrolyte. This effect is very strong for the groups

in direct contact with the surface (these groups are no longer available for metal ion adsorption), but it is only weak for the segments protruding in the solution. The overall result is that the metal ion adsorptivity to the polyelectrolyte in the complex is reduced significantly as compared to that of the "free" polyelectrolyte.

This analysis shows that metal ion binding to the humic acid hematite complex in excess of the simple additivity can only be explained by increased binding to the reactive sites present on the metal oxide. A lower metal ion adsorption to the complex than predicted by the additivity rule will be mainly due to a lower binding to the humic acid. Which of these two effects dominates depends largely on the pH of the system.

At pH 4, the effect of the potential adjustment on the cadmium adsorption on hematite may be substantial, but the total cadmium ion adsorption onto hematite is still negligibly small as compared to the cadmium ion binding to the humic. The cadmium ion binding at pH 4 will thus be dominated by the cadmium ion binding to the adsorbed humic. At low pH values, the highly positive hematite surface "removes" a significant number of mainly carboxylic groups of the humic acid for cadmium ion adsorption. This explains why the cadmium binding is lower than to the "free" humic acid.

At pH 6, a similar reasoning indicates that the cadmium ion binding to the adsorbed humic acid is moderately affected, and again cadmium ion adsorption values lower than to "free" humic are expected. The increased cadmium ion binding to the complex observed at this pH as compared to the noninteracting sum must be the result of a considerable increase of the adsorptivity to the hematite surface due to the screening of the surface charge by the adsorbed humic acid.

At pH 9, a relatively small fraction of the available humic acid groups is bound to the surface, and the cadmium ion binding to the humic is only weakly affected. However, the adsorbed humic acid causes a significant negative electric field around the hematite. Therefore, the cadmium ion binding to hematite in the presence of PAHA will be considerably higher than that at the bare hematite surface at pH 9. This explains the substantial increase in cadmium ion binding at pH 9 as compared to that predicted by the additivity rule (Figure 4c).

Further Illustration of the Model. To corroborate our line of reasoning, the binding of copper(II) to a mixture of humic acid and goethite, as reported by Robertson, will now be discussed. Robertson measured the copper ion adsorption to free humic acid (44), free goethite (45), and the complex (4, 23) at pH 4, 5, and 6 for two different salt concentrations (0.1 and 0.01 M NaClO$_4$) and for three humic acid goethite ratios (0.1:2, 0.1:10, and 0.1:100 w/w). The dependence of the copper ion adsorption on the conditions was comparable to our results, e.g., an increased adsorption with increasing pH. However, a major difference was reported as well. At all pH values the actual copper ion adsorption to the mixture was lower than or equal to that predicted by the additivity rule. The difference at pH 4 with low copper ion adsorptivities was very large, binding decreased to only 15% of that predicted, and it approaches additivity as total copper ion adsorption increases (pH 6 and pCu 4).

These results can be explained with the same reasoning as above. At pH values up to 6, the negative effects (less sites available and a less negative potential near the humic acid groups) are apparently stronger than the positive effects (potential near the goethite surface less positive). That copper ion adsorption shows a stronger decrease than cadmium ion adsorption can also be explained. The binding of copper ions to humic acid is much stronger than that of cadmium ions. Therefore, the contribution of the oxide to the copper

ion adsorption has to be shifted very strongly to become of significance relative to the strong decrease in binding to humic acid and apparently this is not the case. The results of Robertson can thus qualitatively be explained on the basis of the same rules as used for the present results.

An additional aspect not mentioned so far is the type of binding of the metal ion to the humic acid. It might be important that binding of copper ions to humic acid is most probably of bidentate nature, whereas that of cadmium ions is predominantly monodentate (*38*, *46*). This difference in the binding mechanism of the two metal ions results in a more negative effect of binding to humic acids bound to the oxide surface for copper ion adsorption.

Summarizing, the adsorption of a specific metal ion to a humic acid−mineral oxide complex can be qualitatively predicted. Due to the interaction between the negatively charged humic acid and the positive metal oxide, the adsorption of metal ions to the metal oxide in the complex will be increased as compared to that on the isolated oxide, whereas the adsorption to the humic acid in the complex will be decreased as compared to that of the isolated humic. As a result, the overall adsorption of a specific metal ion to the complex will be smaller than predicted by the additivity rule when the metal ion has a more pronounced affinity for the humic than for the mineral oxide (in general this will be the case at low pH). When the metal ion has a higher affinity for the mineral oxide than for the humic acid, the adsorption to the complex will be larger than predicted by the additivity rule (in general this will be the case at high pH).

Acknowledgments

Literature Cited

(1) Laxen, D. P. H. *Water Res.* **1985**, *19*, 1229.
(2) McLaren, R. G.; Lawson, D. M.; Swift, R. S. *J. Soil Sci.* **1986**, *37*, 413.
(3) Tipping, E.; Griffith, J. R.; Hilton, J. *Croat. Chem. Acta* **1983**, *56*, 613.
(4) Robertson, A. P.; Leckie, J. O. In *Humic Substances in the Global Environment and Implications on Human Health*; Proceedings of the 6th International Meeting of the International Humic Substances Society; Senesi, N., Miano, T. M., Eds.; Elsevier: Amsterdam, 1994; p 487.
(5) Bibak, A. *Commun. Soil Sci. Plant Anal.* **1994**, *25*, 3229.
(6) Dzombak, D. A.; Fish, W.; Morel, F. M. M. *Environ. Sci. Technol.* **1986**, *20*, 669.
(7) Tipping, E. *Colloids Surf. A* **1993**, *73*, 117.
(8) Westall, J. C.; Jones, J. D.; Turner, G. D.; Zachara, J. M. *Environ. Sci. Technol.* **1995**, *29*, 951.
(9) Marinsky, J. A.; Reddy, M. M.; Ephraim, J. H.; Mathuthu, A. S. *Anal. Chim. Acta* **1995**, *302*, 309.
(10) Milne, C. J.; Kinniburgh, D. G.; De Wit, J. C. M.; Van Riemsdijk, W. H.; Koopal, L. K. *J. Colloid Interface Sci.* **1995**, *175*, 448.
(11) Kinniburgh, D. G.; Van Riemsdijk, W. H.; Koopal, L. K.; Benedetti, M. F. In *Adsorption of metal ions by Geoderma*; Jenne, E. A., Ed.; Academic Press: San Diego, 1998; p 483.
(12) Vermeer, A. W. P. Ph.D. Thesis, Wageningen Agricultural University, The Netherlands, 1996.
(13) Schindler, P.; Stumm, W. In *Aquatic surface chemistry*; Stumm, W., Ed.; Wiley: New York, 1987.
(14) Fokkink, L. G. J.; De Keizer, A.; Lyklema, J. *J. Colloid Interface Sci.* **1987**, *118*, 454.
(15) Ardizzone, S.; Formaro, L.; Lyklema, J. *J. Electranal. Chem.* **1982**, *133*, 147.
(16) Benjamin, M. M.; Leckie, J. O. *J. Colloid Interface Sci.* **1981**, *79*, 209.
(17) Djafer, M.; Lamy, I.; Terce, M. *Prog. Colloid Polym. Sci.* **1989**, *79*, 150.
(18) Johnson, B. B. *Environ. Sci. Technol.* **1990**, *24*, 112.
(19) Fokkink, L. G. J.; De Keizer, A.; Lyklema, J. *J. Colloid Interface Sci.* **1990**, *135*, 118.
(20) Fokkink, L. G. J. Wageningen Agricultural University, The Netherlands; Unpublished results, 1990.
(21) Venema, P.; Hiemstra, T.; Van Riemsdijk, W. H. *J. Colloid Interface Sci.* **1996**, *183*, 515.
(22) Venema, P.; Hiemstra, T.; Van Riemsdijk, W. H. *J. Colloid Interface Sci.* **1996**, *181*, 45.
(23) Robertson A. P. Ph.D. Thesis, Stanford University, 1996.
(24) Ephraim, J. H.; Ledin, A.; Allard, B. *Sci. Total Environ.* **1989**, *81/82*, 653.
(25) Taylor, M. D.; Theng, B. K. G. *Commun. Soil Sci. Plant Anal.* **1995**, *26*, 765.
(26) Ephraim, J. H.; Allard, B. *Ion Exch. Solvent Extr.* **1993**, *11*, 335.
(27) Davis, A. P.; Bhatnagar, V. *Chemosphere* **1995**, *30*, 243.
(28) Ho, C. H.; Miller, N. H. *J. Colloid Interface Sci.* **1985**, *106*, 281.
(29) Vermeer, A. W. P.; Koopal, L. K. *J. Colloid Interface Sci.* **1999**, *212*, 176.
(30) Vermeer, A. W. P.; Van Riemsdijk, W. H.; Koopal, L. K. *Langmuir* **1998**, *14*, 2810.
(31) Breeuwsma, A.; Lyklema, J. *Discuss. Faraday Soc.* **1971**, *52*, 324.
(32) Kinniburgh, D. G.; Milne, C. J. *Guide to the Wallingford Titrator*; Technical Report WD/93/23; British Geological Survey: Keyworth, Nottinghamshire, U.K., 1993.
(33) Kinniburgh, D. G.; Milne, C. J.; Venema, P. *Soil Sci. Soc. Am. J.* **1995**, *59*, 417.
(34) Van der Lee, J. J.; Temminghoff, E.; Houba, V. J. G.; Novazamsky, I. *Appl. Spectrosc.* **1987**, *41*, 388.
(35) Rusch, U.; Borkovec, M.; Daicic, J.; Van Riemsdijk, W. H. *J. Colloid Interface Sci.* **1997**, *191*, 247.
(36) Perona, M. J.; Leckie, J. O. *J. Colloid Interface Sci.* **1985**, *106*, 64.
(37) Benedetti, M. F.; Milne, C. J.; Kinniburgh, D. G.; Van Riemsdijk, W. H.; Koopal, L. K. *Environ. Sci. Technol.* **1995**, *29*, 446.
(38) Van Riemsdijk, W. H.; De Wit, J. C. M.; Mous, S. L. J.; Koopal, L. K.; Kinniburgh, D. G. *J. Colloid Interface Sci.* **1996**, *183*, 35.
(39) Van Riemsdijk, W. H.; De Wit, J. C. M.; Koopal, L. K.; Bolt, G. H. *J. Colloid Interface Sci.* **1987**, *116*, 511.
(40) Keizer, M.; Van Riemsdijk, W. H. *ECOSAT: A computer program for the calculation of speciation and transport*; Department of Soil Science & Plant Nutrition, Wageningen Agricultural University: Wageningen, The Netherlands, 1996.
(41) Vermeer, A. W. P.; Koopal, L. K. *Langmuir* **1998**, *14*, 4210.
(42) Avena, M. J.; Koopal, L. K. *Environ. Sci. Technol.* **1998**, *32*, 2572.
(43) Vermeer, A. W. P.; Leermakers, F. A. M.; Koopal, L. K. *Langmuir* **1997**, *13*, 4413.
(44) Robertson, A. P.; Leckie, J. O. *Environ. Sci. Technol.* **1999**, *33*, 786.
(45) Robertson, A. P.; Leckie, J. O. *Environ. Sci. Technol.* **1998**, *32*, 2519.
(46) Kinniburgh, D. G.; Milne, C. J.; Benedetti, M. F.; Pinheiro, J. P.; Filius, J.; Koopal, L. K.; Van Riemsdijk, W. H. *Environ. Sci. Technol.* **1996**, *30*, 1687.