

COMPETITIVE ADSORPTION OF Cd AND DYES TO KAOLINITE

RODNEY G. HARRIS[†], BRUCE B. JOHNSON AND JOHN D. WELLS*

Colloid and Environmental Chemistry Laboratory, La Trobe University, PO Box 199, Bendigo, Victoria 3552, Australia

Abstract—The competitive adsorption to kaolinite between Cd(II) and four polyaromatic dyes (9-aminoacridine, 3,6-diaminoacridine, azure A and safranin O) was studied in 5 mM KNO₃ at 25°C. Under these conditions, Cd adsorbs to the silica face of kaolinite between about pH 4 and 6.5, but at higher pH, adsorbed Cd is progressively relocated to the crystal edges. In the presence of dye, less Cd adsorbed to kaolinite below pH 7. If sufficient dye was added to saturate the kaolinite surface, Cd adsorption was totally suppressed up to ~pH 6. At higher pH, Cd followed the characteristic pattern for edge adsorption. In separate experiments 9-aminoacridine and azure A displaced pre-adsorbed Cd from kaolinite. The displacement curves were initially linear, with one Cd ion being displaced for every 13 dye molecules adsorbed at pH 5.5, and one Cd ion for every 35 dye molecules at pH 7.5. The interpretation of these results is that the dyes bind to kaolinite much more strongly than Cd(II) does, but only to the silica face.

Key Words—9-aminoacridine, 3,6-diaminoacridine, Azure A, Clay, Displacement, Dye, Isotherm, Kaolin, Safranin O.

INTRODUCTION

Certain dyes have been shown (Harris *et al.*, 2001, 2006a) to adsorb selectively to kaolinite in preference to hydrous metal oxides. In this paper we report a study of the competitive adsorption between four dyes (9-aminoacridine (9-Aa), 3,6-diaminoacridine (3,6-Daa), azure A (Az-A) and safranin O (Saf-O)) and a heavy metal ion (Cd²⁺) to kaolinite, and the ability of dyes to displace pre-adsorbed Cd from the kaolinite surface. The results provide further information about the nature of the adsorption of the dyes to kaolinite.

Competitive or selective adsorption has been the topic of a number of studies (Benjamin and Leckie, 1981; Margulies *et al.*, 1988; Rytwo *et al.*, 1993; Breen and Rock, 1994), in which multiple adsorbates vied for adsorption sites. Others (Davis and Leckie, 1978; Stadler and Schindler, 1993; Ali and Dzombak, 1996; Angove *et al.*, 1999; Lackovic *et al.*, 2004) have measured the effect of organic molecules on the adsorption of heavy metals to clays and hydrous metal oxides, but few have examined the removal of a pre-adsorbed solute by a second adsorbate (Rytwo *et al.*, 1991).

Competitive adsorption between cations and organic molecules has been studied because of its relevance to the movement of heavy metals in natural systems. While metal cations and molecules such as benzene carboxylic acids have comparable affinities for mineral surfaces (Angove *et al.*, 1999), that is not the case for metal cations and dyes. For example, adsorption of methylene

blue and crystal violet has been used to estimate the CEC of montmorillonite because those dyes remove virtually all pre-adsorbed metal cations from the mineral surface (Rytwo *et al.*, 1991). The authors allowed a metal cation to adsorb to montmorillonite and then methylene blue or crystal violet was added to remove the cation from the surface. The amount of cation so removed was used to calculate the CEC of the mineral. The same research group also found (Margulies *et al.*, 1988) that Cs could not compete with thioflavin T for adsorption to montmorillonite, and (Rytwo *et al.*, 1993, 1995) that binding coefficients for adsorption of organic dyes such as crystal violet, methylene blue, thioflavin T and acriflavine on montmorillonite were up to six orders of magnitude greater than those for metal cations (Na⁺ and Cd²⁺) on the same substrate.

Competitive adsorption between metal cations such as Cu, Pb, Zn and Cd has also been studied extensively (Benjamin and Leckie, 1981; Zachara and Smith, 1994; Palmqvist *et al.*, 1999; Christl and Kretzschmar, 1999), but this competition tends not to lean so heavily in the favor of one adsorbate as it does for competition between dyes and metals.

Our previous work (Harris *et al.*, 2001, 2006a) strongly indicated that the four dyes under study adsorb to the silica face of kaolinite, and that they do so much more strongly than heavy metal ions. It is also known that the adsorption of metal ions such as Cd²⁺ to the face and edges of kaolinite can be controlled by manipulation of pH and ionic strength. The adsorption behavior of Cd on kaolinite has been investigated extensively and is well understood (Schindler *et al.*, 1987; Spark *et al.*, 1995; Angove *et al.*, 1997, 1998, 1999), making Cd an ideal probe for use in this study.

Adsorption of Cd to kaolinite increases from pH 3 to 10 with a stepped curve (Schindler *et al.*, 1987; Spark *et*

* E-mail address of corresponding author:

j.wells@latrobe.edu.au

[†]Present address: Brewing Research International, Lyttel Hall, Nutfield, Surrey RH1 4HY, UK
DOI: 10.1346/CCMN.2006.0540405

al., 1995; Angove *et al.*, 1997). Surface complexation modelling has shown that adsorption to the kaolinite face increases from zero at pH 3.5 to a maximum around pH 6.5, and then decreases almost to zero at pH 10. Adsorption to the kaolinite edge increases from zero at around pH 6 to a maximum about pH 9.5, where it reaches a plateau (Schindler *et al.*, 1987; Spark *et al.*, 1995; Angove *et al.*, 1997).

Ionic strength is another control on the adsorption of Cd to kaolinite because of competition between Cd^{2+} and the cations (Na^+ or K^+) of the background electrolyte (Spark *et al.*, 1995). At low ionic strength (e.g. 5 mM), Cd can adsorb to the face or edge of kaolinite, but at high ionic strength (e.g. 100 mM) it can adsorb only to the kaolinite edge, regardless of the pH (Angove *et al.*, 1997), because K^+ ions occupy exchange sites on the faces of the particles.

By manipulating pH and ionic strength, and studying the competitive adsorption between Cd^{2+} and dyes, we have been able to gain another perspective on the adsorption of dyes to kaolinite. First, from estimates of the speciation of Cd(II) in the presence of 9-Aa obtained from ion-selective electrode data we showed that insignificant amounts of Cd-dye complex formed in solution. Next, from measurements of the adsorption of Cd in the presence of the four dyes as a function of pH, we found further evidence that the dyes adsorbed only to the kaolinite face. Finally, the ability of 9-Aa and Az-A to displace Cd^{2+} from the surface of kaolinite was exploited to highlight the affinity of the dyes for the kaolinite face and to give an indication of the size of the dye aggregates.

The Cd adsorption data have been interpreted with the aid of a surface complexation model, but the development of a quantitative model for dye adsorption has been left to a separate paper (Harris *et al.*, 2006b).

MATERIALS AND METHODS

Materials

9-Aminoacridine hydrochloride hydrate (52417-22-8; 98%), 3,6-diaminoacridine hydrochloride (952-23-8; 95%), azure A (531-53-3; 98%) and safranin O (477-73-6; 96%) were obtained from Sigma. Other reagents were of analytical reagent grade. Fresh stock solutions of the dyes (5 mM for 9-Aa and 3,6-Daa; 2 mM for Az-A and Saf-O) were prepared weekly and stored in borosilicate glass vessels in the dark. Milli-Q[®] reagent-grade water (Millipore Corp., Bedford, USA) was used throughout.

Acid-washed kaolinite (Ajax Chemicals, Sydney, Australia), as used in several previous studies (Harris *et al.*, 2001, 2006a; Angove *et al.*, 1997, 1998, 1999; Lackovic *et al.*, 2003a, 2003b) was used without further treatment. X-ray diffraction data (Philips PW1710 X-ray diffractometer fitted with a Cu target) showed that it was highly crystalline, with a basal (d_{001}) spacing of 7.17 Å.

Scanning electron micrographs (Cambridge S150 Stereoscan) showed hexagonal plate-like crystals ~1.5–2 µm across and ~0.2 µm thick. The BET surface area (measured on a Micromeritics AP2000 instrument after out-gassing at room temperature for 16 h) was $14.7 \pm 0.1 \text{ m}^2 \text{ g}^{-1}$.

Measurement of pH

Orion Ross Sure-Flow double junction combined pH electrodes (with outer reference electrolyte 0.1 M KNO_3) and Metrohm 632 pH meters were calibrated with NBS standard buffers (pH 4.01, 6.86 and 9.18) before and after each experiment. Experimental results were accepted only if the initial and final calibrations agreed within 0.05 pH units.

Cd-dye complexation

A solution containing 1 mM Cd^{2+} plus 1 mM dye was prepared in 10 mM KNO_3 . The concentration of Cd^{2+} was measured at 25°C ($\pm 0.5^\circ\text{C}$) over the pH range 3–10 by use of a Cd ion selective electrode (Orion combination 9648 'Sure Flow' electrode, the outer junction of which was filled with 17% KNO_3 + 5% KCl solution) and an Orion 720A pH meter. Cd^{2+} standards, in the range 0–1 mM, were prepared from analytical grade $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, in 10 mM KNO_3 in order to match the ionic strength of the experiments. The Cd electrode was re-calibrated at the conclusion of the experiment to check that the response had not changed by more than 5%.

Determination of adsorbates

Samples were centrifuged at 12,000 g for 15 min, and the supernatant solutions assayed for dye, Cd(II), or both, as required. To determine dye concentrations, the supernatant solutions were diluted with buffer to give absorbances of <1, and the absorbances measured in a Varian DMS-80 UV-visible spectrophotometer (at 400 nm for 9-Aa; at 443 nm for 3,6-Daa; at 622 nm for Az-A; at 518 nm for Saf-O). Linear calibration curves were constructed from absorbance measurements of stock solutions diluted in the same manner. Phthalate buffer (pH 4.01) was used to dilute 3,6-Daa solutions, and borax buffer (pH 9.18) was used for the other dyes.

Total Cd(II) was determined by flame atomic absorption spectrophotometry (Varian SpectrAA 10). $\text{Cd}(\text{NO}_3)_2$ standards were prepared in acid solution and measured at 226.5 nm.

Adsorption experiments

Adsorption experiments were performed, in duplicate, in borosilicate glass reaction vessels under an atmosphere of CO_2 -free nitrogen. Reaction mixtures were stirred continuously and maintained at 25°C ($\pm 0.5^\circ\text{C}$) by water circulated from a thermostated bath through the jacket of the reaction vessel. Except where stated otherwise, the background electrolyte was 10 mM KNO_3 . Before any experiment involving suspended

kaolinite, the mineral particles were hydrated for at least 18 h in a stirred, CO₂-free suspension.

The pH of a suspension of pre-hydrated kaolinite (8, 10 or 100 m²L⁻¹) in 10 mM KNO₃ was decreased to ~3.5 with a measured quantity of 1 M HNO₃. Adsorbate stock solution was added to give the desired total concentration, and the suspension equilibrated for a further 30 min. A sample was taken and centrifuged, and the supernatant solution assayed for adsorbate. Then KOH was added to the remaining suspension to raise the pH by ~0.5, the suspension was re-equilibrated for 15–20 min and another sample was taken. (Preliminary experiments showed that the concentration of adsorbate in solution became constant within 15 min.) This process was repeated until the pH of the suspension was ~10.5 for Cd(II) adsorption, or 12 for dye adsorption.

In some experiments both Cd(II) (50 μM) and dye (either 100 μM, or 500 to 900 μM) were added to the kaolinite suspension. The supernatant solutions from samples were assayed for both adsorbates. In these experiments the background electrolyte was 5 mM KNO₃.

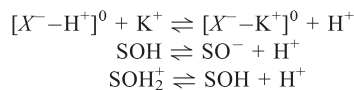
Displacement of adsorbed cadmium by dye

The pH of a pre-hydrated suspension of kaolinite (100 m²L⁻¹) in 5 mM KNO₃ was adjusted to 5.5 or 7.5, and then maintained at the same pH by the addition of acid or base from a PC-controlled piston burette (Metrohm 655). Cadmium stock solution was added to give a total Cd concentration of 50 μM. The system was equilibrated for 30 min and a sample taken. A measured volume of dye stock solution was then added to the suspension to give a dye concentration of ~70 μM. The system was equilibrated for 15 min and another sample taken. Further additions of dye were made, with subsequent sampling, until the total dye concentration was ~700 μM. The samples were centrifuged and the supernatant solutions assayed for both Cd and dye.

MODELING OF Cd ADSORPTION

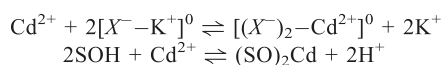
Adsorption of Cd to kaolinite was modeled by an extended constant capacitance surface complexation model much like that used by Angove *et al.* (1997) and Lackovic *et al.* (2003a), and similar to that of Schindler *et al.* (1987). Values of equilibrium constants for the model reactions were estimated by the use of *GrFit* software (Ludwig, 1996). Equilibrium constants and surface-site densities were first determined for the protonation and deprotonation of the kaolinite surface by modeling potentiometric titration data. These values were then introduced as fixed values when modeling data for adsorption at varying pH for Cd-mineral systems.

Surface protonation of kaolinite was modeled by three reactions:



where X^- represents a permanent negative charge on the basal face of kaolinite, and $[X^- - K^+]^0$ and $[X^- - H^+]^0$ denote outer-sphere complexation of a K⁺ ion (from the background electrolyte) and a proton to an X^- site, respectively. SOH is a surface hydroxyl group on the edge of the kaolinite crystal. Although no distinction is made between aluminol (AlOH) and silanol (SiOH) surface groups, it is likely that the SOH groups involved in protonation, deprotonation and adsorption are mostly AlOH (Schindler *et al.*, 1987; Spark *et al.*, 1995).

Cd²⁺ adsorption was modeled by two surface reactions:



where $[(X^-)_2 - Cd^{2+}]^0$ represents outer-sphere complexation of Cd²⁺ with two X^- charges, and $(SO)_2Cd$ denotes a bidentate inner-sphere complex at the crystal edge.

RESULTS AND DISCUSSION

Cd speciation in the presence of 9-amino acridine

Possible complexation of Cd²⁺ by 9-aminoacridine was investigated by titrating 1 mM Cd(II) solutions, with or without added 1 mM 9-aminoacridine, over the pH range 4–10. The concentration of Cd²⁺ was monitored by use of a Cd-selective electrode. The results, in Figure 1, show that the presence of 9-aminoacridine had almost no effect on the concentra-

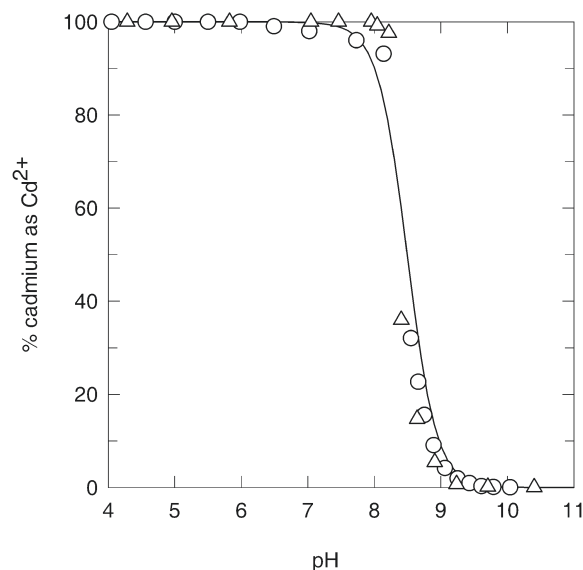


Figure 1. Effect of 9-aminoacridine on the hydrolysis of Cd²⁺. The points show the concentration of Cd²⁺ (Δ) in 1 mM Cd(II) solution, and (○) in 1 mM Cd(II) plus 1 mM 9-Aa. Background electrolyte 5 mM KNO₃. The line represents the concentration of Cd²⁺ calculated from data of Baes and Mesmer (1976).

tion of Cd^{2+} . Free Cd^{2+} was the dominant Cd species up to pH 8, above which the concentration of Cd^{2+} decreased rapidly as first CdOH^+ formed between pH 8 and 9, followed by $\text{Cd}(\text{OH})_2$ precipitate, clearly visible during the experiment, at higher pH (Baes and Mesmer, 1976).

Distribution of Cd^{2+} in the presence of 9-Aa closely followed that for Cd alone, and in both cases the results corresponded to those (solid line in Figure 1) calculated from hydrolysis data of Baes and Mesmer (1976). This is good evidence that Cd and 9-aminoacridine do not form significant complexes in solution. The slight difference in $\% \text{Cd}^{2+}$ between pH 6 and 8 may indicate weak complex formation, but it is close to the limit of experimental precision.

Cd adsorption at high and low ionic strength

Figure 2 shows adsorption of $50 \mu\text{M}$ Cd to kaolinite in the presence of 5 mM and 100 mM KNO_3 . The broad lines in Figure 2a are empirical lines of best fit to the data, reproduced in Figure 3 to allow comparison between data for Cd adsorption from simple salt solutions and those for Cd adsorption in the presence of dye. In Figure 2b the experimental data have been fitted to the surface complexation model, the model parameters of which are listed in Table 1. The table also shows parameter estimates from previous work which are close to those of the current study.

The stepped curve for the lower ionic strength data (Figure 2a) indicates that two distinct processes are involved in the adsorption (Spark *et al.*, 1995; Angove *et al.*, 1997; Lackovic *et al.*, 2003a). The model curves in Figure 2b show that these are adsorption to silica faces ($\sim\text{pH}$ 4–8) and to edges sites ($\sim\text{pH}$ >7). At the greater ionic strength the experimental data follow the edge-only model line, because Cd adsorption at the faces is almost completely suppressed by competition from K^+ ions from the electrolyte (Spark *et al.*, 1995; Angove *et al.*, 1997).

Cd adsorption in presence of dyes

Because the solubility of the dyes decreases rapidly as the ionic strength increases (Harris *et al.*, 2001), dye adsorption experiments could be conducted only at low ionic strength. We selected 5 mM KNO_3 as the background electrolyte in order to keep the ionic strength approximately constant as the pH was varied. Knowing that in 5 mM KNO_3 , Cd adsorbs only to the silica faces at low pH (Fig. 2), we were able to test whether the dyes could compete for face sites by looking at the extent to which Cd adsorption was suppressed below $\sim\text{pH}$ 7. Competition from dyes at the edge sites could be assessed by comparison with the Cd adsorption data for 100 mM KNO_3 (Figure 2), as, in those experiments, Cd adsorbed only at the edge sites.

Adsorption of Cd to kaolinite at low ionic strength (5 mM KNO_3) was measured in the presence of low

(100 μM) and high concentrations of each dye. The high concentrations were sufficient to bring the kaolinite surface close to saturation: 500 μM 9-Aa; 650 μM 3,6-Daa; 700 μM Az-A; 900 μM Saf-O. Figure 3 shows the results, together with the lines from Figure 2a that represent the adsorption of Cd without dye at both low (5 mM) and high (100 mM) ionic strengths.

The adsorption of Cd was significantly reduced when dye was present. At low dye concentration (100 μM), less Cd adsorbed below pH 7, where Cd adsorbs to the kaolinite face. This shows that the dyes competed successfully with Cd for permanently charged adsorption sites on the kaolinite face. At the higher dye concentrations (corresponding approximately to the maximum

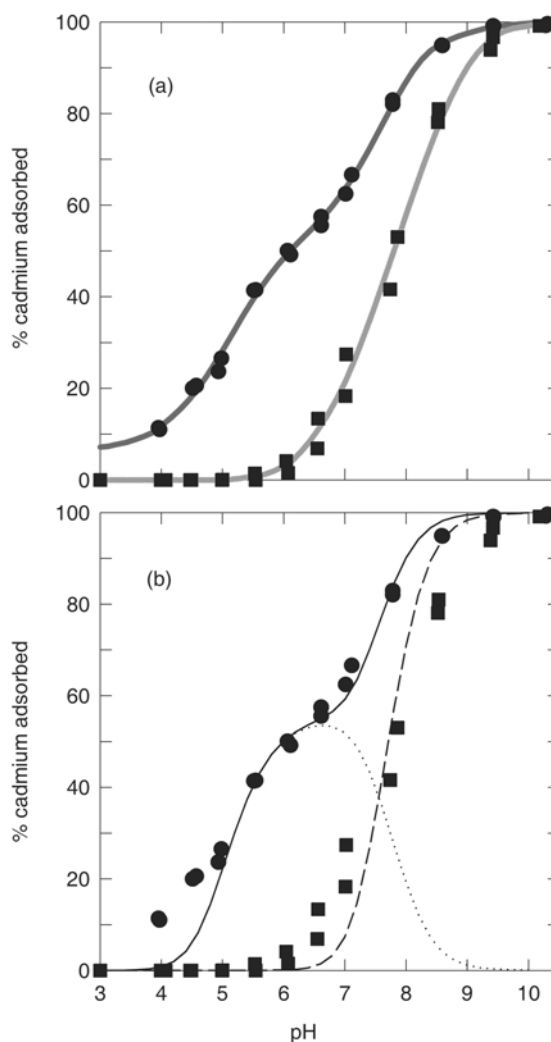


Figure 2. Adsorption of Cd ($50 \mu\text{M}$) to kaolinite in (●) 5 mM and (■) 100 mM KNO_3 . (a) — and — represent empirical lines of best fit to the data. (b) Speciation diagram showing surface species, estimated from the surface complexation model with parameters in Table 1: ····· adsorption to the kaolinite face; — adsorption to the kaolinite edge; — total adsorption (edge + face). [Kaolinite] = $100 \text{ m}^2 \text{ L}^{-1}$.

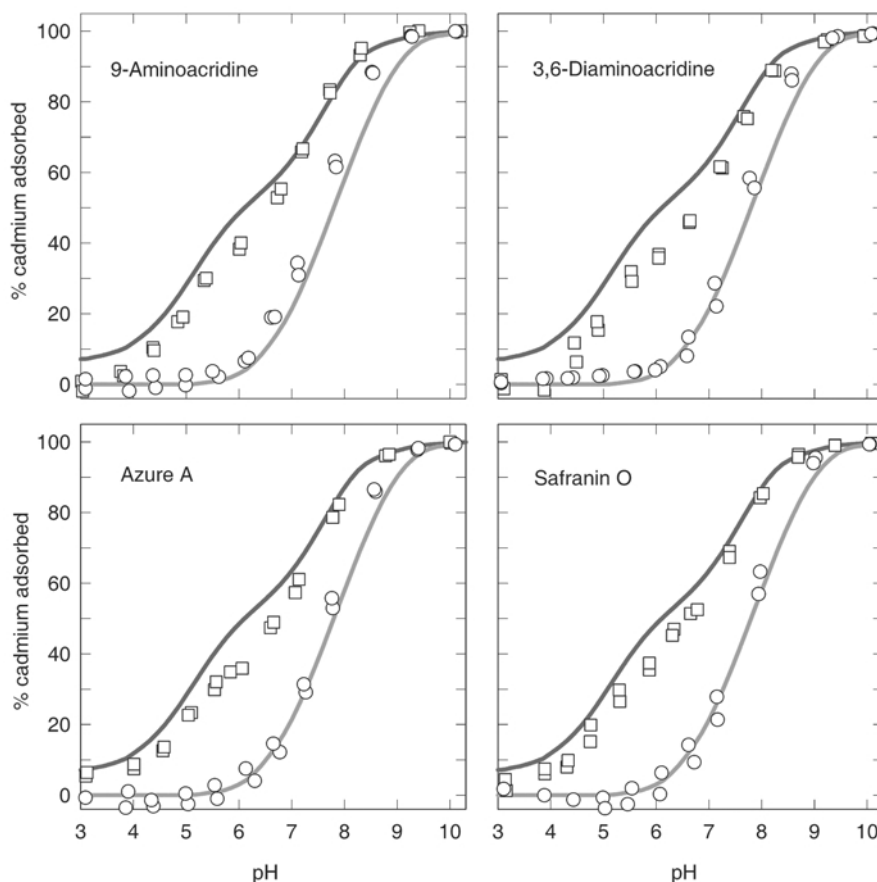


Figure 3. Adsorption of Cd (50 μM) to kaolinite in the presence of dyes: (\square) [dye] = 100 μM ; (\circ) [dye] = 500–900 μM (500 μM 9-Aa; 650 μM 3,6-Daa; 700 μM Az-A; 900 μM Saf-O); \blacksquare and \blacksquare are lines of best fit for Cd adsorption in the absence of dye at 5 mM and 100 mM KNO_3 , respectively (Figure 2a). [Kaolinite] = 100 m^2L^{-1} ; [KNO_3] = 5 mM.

loading for each dye) the Cd adsorption curves closely follow that for adsorption to the kaolinite edge only (as seen in Figure 2 for Cd adsorption without dye in 100 mM KNO_3), suggesting that virtually no Cd can adsorb to the face sites, as they are preferentially covered with dye molecules. This reaffirms the contention that dye adsorption is only to the kaolinite face.

The adsorption of dye was also measured in these experiments. The data (which are not presented here) were almost identical to those for adsorption from solutions of dye alone, indicating that Cd had very little effect on the adsorption of the dyes to kaolinite, consistent with our earlier observation (Harris *et al.*, 2006a) that the dyes adsorb to kaolinite much more strongly than heavy metals do.

Displacement of Cd by dyes

Having established that the four selected dyes can greatly reduce the adsorption of Cd to kaolinite, we further investigated the competitive adsorption by testing the displacement of pre-adsorbed Cd by dye.

Cadmium (50 μM) was first added to a kaolinite suspension and allowed to equilibrate, after which the

concentration of 9-Aa or Az-A was progressively increased. After each addition of dye, the amounts of dye and Cd adsorbed were estimated from their remaining concentrations in solution: see Figure 4. At pH 5.5, ~50% of the Cd was adsorbed in the absence of dye, to give a coverage of 0.25 $\mu\text{mol m}^{-2}$; this was reduced to 2% by addition of ~400 μM of dye. At pH 7.5, ~75% of the added Cd was adsorbed in the absence of dye, to give a surface loading of 0.38 $\mu\text{mol m}^{-2}$; this was reduced to 50% by addition of 400 μM of dye. The final amount of dye adsorbed in each case corresponded to a coverage of at least a monolayer (Harris *et al.*, 2001) on the kaolinite face.

The surface complexation model showed (Figure 2b) that at pH 5.5, Cd is adsorbed solely to the kaolinite faces. Addition of 9-Aa or Az-A initially resulted in the removal of one Cd ion, on average, for every 13 dye ions adsorbed (as indicated by the slope of the line in Figure 4 up to 3.3 $\mu\text{mol m}^{-2}$ of dye adsorbed). If 13 dye molecules are required to remove one adsorbed Cd^{2+} ion, and each Cd occupies two face sites, as proposed by the model, then ~6–7 dye monomers may be considered to adsorb per charged surface site. This might be seen as an

Table 1. Parameters of the extended constant capacitance surface complexation model for the adsorption of Cd(II) to Ajax kaolinite.

pK_w	14.00 ^a		
Formation constants ($\log_{10} K$):			
CdOH^+	-10.08 ^b		
$\text{Cd}(\text{OH})_2$ (aq)	-20.36 ^b		
Surface reactions ($\log_{10} K$):			
$\text{SOH} + \text{H}^+ \rightleftharpoons \text{SOH}_2^+$	This study	Lackovic ^c	Angove ^d
	3.25	3.24	3.24
$\text{SOH} \rightleftharpoons \text{SO}^- + \text{H}^+$	-6.86	-7.55	-7.15
$[\text{X}^- - \text{H}^+]^0 + \text{K}^+ \rightleftharpoons [\text{X}^- - \text{K}^+]^0 + \text{H}^+$	-2.74	-2.88	-2.88
$\text{Cd}^{2+} + 2[\text{X}^- - \text{K}^+]^0 \rightleftharpoons [\text{X}_2^{2-} - \text{Cd}^{2+}]^0 + 2\text{K}^+$	3.17	3.35	3.01
$2\text{SOH} + \text{Cd}^{2+} \rightleftharpoons (\text{SO})_2\text{Cd} + 2\text{H}^+$	-7.67	-7.35	-7.75
Other parameters:			
Site density XH ($\mu\text{mol m}^{-2}$)	2.0	2.2	2.3
Site density SOH ($\mu\text{mol m}^{-2}$)	3.2	3.0	3.2
Specific capacitance, inner (F m^{-2})	3.0	3.0	
Specific capacitance, outer (F m^{-2})	7.0	7.0	2.1 ^e

^a Lide and Frederiske (1994)

^b Baes and Mesmer (1976)

^c Extended constant capacitance models (Lackovic *et al.*, 2003a, 2004)

^d Constant capacitance models (Angove *et al.*, 1997, 1998, 1999)

^e The capacitance used by Angove is equivalent to the combined inner and outer capacitances used in this study and by Lackovic: $1/C_{\text{total}} = 1/C_{\text{inner}} + 1/C_{\text{outer}}$.

indication of the average size of the adsorbed aggregates: however, it should be taken as a maximum estimate, as adsorbed dye molecules may not be confined to the charged surface sites.

Fitting of data for the separate sorption of the dyes and Cd at pH 5.5 by the Langmuir isotherm (Harris, 2004; Harris *et al.*, 2006a) gave estimates for the

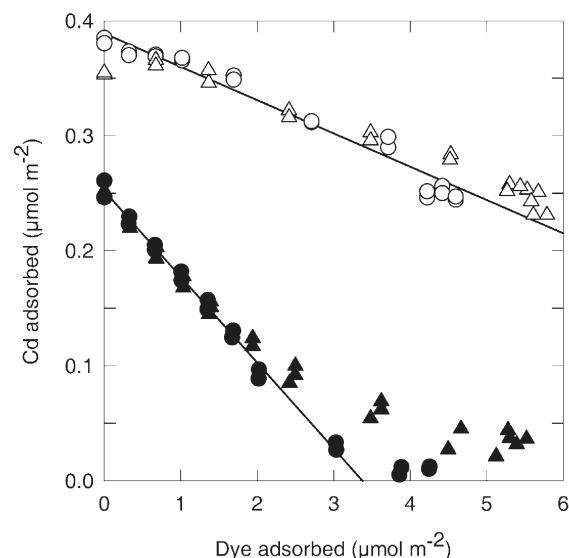


Figure 4. Displacement of Cd (50 μM) from kaolinite by (○) 9-aminoacridine and (△) azure A, at pH 5.5 (filled symbols) and 7.5 (open symbols). The lines represent linear regression of the data at lower dye concentrations (up to 3.3 $\mu\text{mol m}^{-2}$).

maximum adsorption densities (N_m) of 9-Aa and Az-A that were 5.4 times and 6.5 times that of Cd, respectively, in agreement with the value of 6–7 obtained from the displacement experiments.

The ratio of dye adsorbed to Cd displaced is much higher at pH 7.5 (~35 rather than 13). At this pH, only about half of the initially adsorbed Cd was located on the silica faces (Figure 2b), but because the dyes adsorb only to the face they cannot displace Cd from the edges. Furthermore, Cd displaced from the face may re-adsorb to the edges, masking the effect of its displacement from the face. It is also possible that the dyes adsorb as larger aggregates at the higher pH (Harris *et al.*, 2006a).

At pH 5.5, the adsorption of 9-Aa and removal of Cd from the kaolinite face followed a linear relationship until very little adsorbed Cd remained. A similar linear relationship was found for Az-A, but it did not persist to such a low Cd concentration. We might speculate that the more bulky Az-A molecules form more open layers on the kaolinite face, allowing a larger amount of Cd to remain adsorbed, or that the sizes of the adsorbing 9-Aa and Az-A aggregates may be different, but there is no direct evidence by which those suggestions can be tested.

CONCLUSIONS

The results presented confirm that the four dyes studied adsorb to the basal face of kaolinite, rather than to the edges of the kaolinite crystals. Because the dyes have a much greater affinity for kaolinite than Cd ions do, they compete effectively for adsorption sites. Two of

the dyes have been shown to displace Cd from kaolinite very efficiently at pH 5.5, but because the dyes do not adsorb to the kaolinite edges, they are less effective at displacing Cd at pH 7.5. The displacement data suggest that ~6–7 dye molecules occupy the same surface area as one Cd ion, consistent with independent estimates obtained from the adsorption of the various adsorbates one at a time.

REFERENCES

- Ali, M.A. and Dzombak, D.A. (1996) Effects of simple organic acids on sorption of Cu^{2+} and Ca^{2+} on goethite. *Geochimica et Cosmochimica Acta*, **60**, 291–304.
- Angove, M.J., Johnson, B.B. and Wells, J.D. (1997) Adsorption of cadmium(II) on kaolinite. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **126**, 137–147.
- Angove, M.J., Johnson, B.B. and Wells, J.D. (1998) The influence of temperature on the adsorption of cadmium(II) and cobalt(II) on kaolinite. *Journal of Colloid and Interface Science*, **204**, 93–103.
- Angove, M.J., Wells, J.D. and Johnson, B.B. (1999) Adsorption of cadmium(II) onto goethite and kaolinite in the presence of benzene carboxylic acids. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **146**, 243–251.
- Baes, C.F.J. and Mesmer, R.E. (1976) *The Hydrolysis of Cations*. John Wiley & Sons, New York.
- Benjamin, M.M. and Leckie, J.O. (1981) Competitive adsorption of Cd, Cu, Zn, and Pb on amorphous iron oxyhydroxide. *Journal of Colloid and Interface Science*, **83**, 410–419.
- Breen, C. and Rock, B. (1994) The competitive adsorption of methylene blue on to montmorillonite from binary solution with thioflavin T, proflavine and acridine yellow. Steady-state and dynamic studies. *Clay Minerals*, **29**, 179–189.
- Christl, I. and Kretzschmar, R. (1999) Competitive sorption of copper and lead at the oxide-water interface: Implications for surface site density. *Geochimica et Cosmochimica Acta*, **63**, 2929–2938.
- Davis, J.A. and Leckie, J.O. (1978) Effect of adsorbed complexing ligands on trace metal uptake by hydrous oxides. *Environmental Science and Technology*, **12**, 1309–1315.
- Harris, R.G. (2004) The differential adsorption of organic molecules to mineral surfaces. PhD Thesis. La Trobe University, Bendigo, Australia.
- Harris, R.G., Wells, J.D. and Johnson, B.B. (2001) Selective adsorption of dyes and other organic molecules to kaolinite and oxide surfaces. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **180**, 131–140.
- Harris, R.G., Johnson, B.B. and Wells, J.D. (2006a) Studies on the adsorption of dyes to kaolinite. *Clays and Clay Minerals*, **54**, 435–448.
- Harris, R.G., Johnson, B.B. and Wells, J.D. (2006b) Modeling the adsorption of organic dye molecules to kaolinite. *Clays and Clay Minerals*, **54**, 456–465.
- Lackovic, K., Angove, M.J., Wells, J.D. and Johnson, B.B. (2003a) Modeling the adsorption of Cd(II) onto Muloorina illite and related clay minerals. *Journal of Colloid and Interface Science*, **257**, 31–40.
- Lackovic, K., Johnson, B.B., Angove, M.J. and Wells, J.D. (2003b) Modeling the adsorption of citric acid onto Muloorina illite and related clay minerals. *Journal of Colloid and Interface Science*, **267**, 49–59.
- Lackovic, K., Wells, J.D., Johnson, B.B. and Angove, M.J. (2004) Modeling the adsorption of Cd(II) onto kaolinite and Muloorina illite in the presence of citric acid. *Journal of Colloid and Interface Science*, **270**, 86–93.
- Lide, D.R. and Frederikse, H.P.R. (1994) *CRC Handbook of Chemistry and Physics*, 75th edition. CRC Press, Boca Raton, Florida.
- Ludwig, C. (1996) *GrFit – A Computer Program for Solving Speciation Problems: Evaluation of Equilibrium Constants, Concentrations and other Physical Parameters*. University of Berne, Switzerland.
- Margulies, L., Rozen, H. and Nir, S. (1988) Model for competitive adsorption of organic cations on clays. *Clays and Clay Minerals*, **36**, 270–276.
- Palmqvist, U., Ahlberg, E., Lövgren, L. and Sjöberg, S. (1999) Competitive metal ion adsorption in goethite systems using *in situ* voltammetric methods and potentiometry. *Journal of Colloid and Interface Science*, **218**, 388–396.
- Rytwo, G., Nir, S. and Margulies, L. (1993) Competitive adsorption of methylene blue and crystal violet to montmorillonite. *Clay Minerals*, **28**, 139–143.
- Rytwo, G., Nir, S. and Margulies, L. (1995) Interactions of monovalent organic cations with montmorillonite: Adsorption studies and model calculations. *Soil Science Society of America Journal*, **59**, 554–564.
- Rytwo, G., Serban, C., Nir, S. and Margulies, L. (1991) Use of methylene blue and crystal violet for determination of exchangeable cations in montmorillonite. *Clays and Clay Minerals*, **39**, 551–555.
- Schindler, P.W., Liechti, P. and Westall, J.C. (1987) Adsorption of copper, cadmium and lead from aqueous solutions to the kaolinite/water interface. *Netherlands Journal of Agricultural Science*, **35**, 219–230.
- Spark, K.M., Wells, J.D. and Johnson, B.B. (1995) Characterizing trace metal adsorption on kaolinite. *European Journal of Soil Science*, **46**, 633–640.
- Stadler, M. and Schindler, P.W. (1993) The effect of dissolved ligands upon the sorption of Cu(II) by Ca-montmorillonite. *Clays and Clay Minerals*, **41**, 680–692.
- Zachara, J.M. and Smith, S.C. (1994) Edge complexation reactions of cadmium on specimen and soil-derived smectite. *Soil Science Society of America Journal*, **58**, 762–769.

(Received 2 August 2005; revised 17 February 2006; Ms. 1076)