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# MODELING THE ADSORPTION OF ORGANIC DYE MOLECULES TO KAOLINITE

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**Abstract**—Simple extended constant capacitance surface complexation models have been developed to represent the adsorption of polyaromatic dyes (9-aminoacridine, 3,6-diaminoacridine, azure A and safranin O) to kaolinite, and the competitive adsorption of the dyes with Cd. The formulation of the models was based on data from recent publications, including quantitative adsorption measurements over a range of conditions (varying pH and concentration), acid-base titrations and attenuated total reflectance-Fourier transform infrared spectroscopic data. In the models the dye molecules adsorb as aggregates of three or four, forming outer-sphere complexes with sites on the silica face of kaolinite. Both electrostatic and hydrophobic interactions are implicated in the adsorption processes. Despite their simplicity, the models fit a wide range of experimental data, thereby supporting the underlying hypothesis that the flat, hydrophobic, but slightly charged silica faces of kaolinite facilitate the aggregation and adsorption of the flat, aromatic, cationic dye molecules.

**Key Words**—9-aminoacridine, 3,6-diaminoacridine, Azure A, Dye, Hydrophobic Interactions, Kaolin, Safranin O, Surface Complexation Models.

## INTRODUCTION

A range of experimental data (Harris *et al.*, 2001, 2006a, 2006b) has shown that certain organic dyes adsorb to kaolinite much more strongly, and to a much greater extent, than to oxide surfaces. The dyes, 9-aminoacridine (9-Aa), 3,6-diaminoacridine (3,6-Daa), azure A (Az-A) and safranin O (Saf-O), are characterized by flat, polyaromatic molecules that carry amino groups, making them cationic over a wide pH range. The data indicate that adsorption is restricted to the somewhat hydrophobic silica faces of kaolinite, which carry a slight but permanent negative charge. The maximum adsorption densities exceed monolayer coverage of the silica faces. On the basis of acid-base titrations, quantitative adsorption measurements, attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectra and measurements of the competitive adsorption of Cd and dyes to kaolinite, we have proposed (Harris *et al.*, 2006a, 2006b) that the dyes adsorb as aggregates to the silica faces of kaolinite, which act as templates for the aggregation of the dye molecules.

This paper reports an attempt to represent the adsorption quantitatively, and shows that the experimental data can be described by simple surface complexation models. Although the models are not completely realistic, they indicate that the hypotheses developed on a qualitative basis can be formulated to give a quantitative description of the dye-kaolinite systems.

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Modeling the adsorption of dyes to mineral surfaces must take into account factors that are less important for metal ion adsorption. For example, metal ions are often regarded as point charges, but because most dyes are large organic molecules in which charges may be distributed over a wide area, the inaccuracies introduced by the point charge assumption are much greater. Furthermore, many dyes are known to aggregate under some conditions, resulting in a physically larger adsorbing species, the concentration of which in solution is less than the formal concentration expressed in terms of the monomer. Aggregation may also occur on the adsorbate surface. Regardless of whether aggregation takes place in solution or at the surface, the adsorbed dye may be present in multiple layers, with a corresponding broad distribution of charge. In particular the surface charge may be reversed. For example, a cationic dye adsorbing to a negatively charged surface site may form a neutral complex, and adsorption of a further dye cation to this would cause the surface to become positively charged.

De *et al.* (1967) found that at small concentrations (below the concentration at which methylene blue forms dimers in solution) adsorption of methylene blue onto kaolinite fitted the Langmuir equation. They argued that adherence to the Langmuir equation suggested monolayer adsorption. While this may be the case, when aggregation occurs, each dye 'particle' or aggregate behaves as a single 'molecule' of the dye (Venkata Rao and Sastry, 1987). Thus, the Langmuir equation should also describe the adsorption of dimers or oligomers, which would give rise to an adsorbed multilayer of dye. We, too, found that the Langmuir equation described the adsorption of dyes to kaolinite under most conditions (Harris *et al.*, 2006a). The resulting estimates of the maximum adsorption densities were used in this work to give initital estimates of parameters for the surface complexation models.

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The models of Nir and co-workers (Nir, 1984; Margulies *et al.*, 1988; Rytwo *et al.*, 1991, 1993, 1995, 1998; Nir *et al.*, 1994, 2000; Polubesova and Nir, 1999) account for the effect of aggregation of dye in solution by use of a term to allow for the effective decrease in solution concentration of dye monomer. Their models also allow for stepwise adsorption of two layers of dye (including competitive adsorption of two different dyes), resulting in charge reversal at the surface.

In this study we chose to adopt a surface complexation modeling approach in preference to that of Nir, as surface complexation models are used widely, and in particular they have been applied to the adsorption of Cd and other transition metals to the same kaolinite sample, allowing direct comparison between this work and other published data. Of the various types of surface complexation model, Extended Constant Capacitance Models (ECCMs) (Nordin *et al.*, 1998; Persson *et al.*, 1998) were selected because they are the simplest surface complexation models that allow for the distribution of charge within the adsorbed layer or layers, in that charges can be allocated to the surface layer (0-plane) for inner-sphere complexes, or the β-plane for outer-sphere complexes. Although triple layer (Davis *et al.*, 1978), or charge distribution models (Venema *et al.*, 1996) could potentially give a more detailed picture of dye adsorption, it is our view that the number of adjustable parameters should be kept to a minimum. A further advantage is that ECCMs have already been used to model adsorption of Cd to kaolinite (Harris *et al.*, 2006b; Lackovic *et al.*, 2003a), which is considered here in the context of the competitive adsorption of dyes and Cd.

## METHODS

### *Materials*

Details are given in previous papers (Harris *et al.*, 2006a, 2006b). The dyes were obtained from Sigma. There were two kaolinite samples. Most experiments used 'Ajax kaolinite' (from Ajax Chemicals, Sydney, Australia), which had a BET surface area of 14.7±0.1 $m^2g^{-1}$. In some experiments 'Comalco kaolinite' (kindly supplied by Comalco Research Laboratories, Melbourne, Australia), with a BET surface area of 28.1±0.1 $m^2g^{-1}$, was used. Comalco kaolinite had thicker crystals of smaller diameter, and a face:edge ratio approximately one third that of Ajax kaolinite.

### *Experiments*

Details are given in previous papers (Harris *et al.*, 2006a, 2006b). The experiments consisted of acid-base titrations of kaolinite suspensions in the presence of dye, adsorption of dye at fixed total concentration but varying pH, adsorption of dye at fixed pH but varying concentration, competitive adsorption of Cd and dye at varying pH, and displacement of pre-adsorbed Cd by added dye.

The background electrolyte was 5 mM or 10 mM $KNO_3$, which served to maintain the ionic strength approximately constant. It was not possible to use much higher ionic strengths because under such conditions the solubilities of the dyes were too low.

### *Modeling of adsorption data*

Data from previous papers (Harris *et al.*, 2006a, 2006b) were modeled by ECC surface complexation models, by use of *GrFit* software (Ludwig, 1996). The model described previously for the sorption of Cd(II) to kaolinite (Harris *et al.*, 2006b) was augmented by the addition of reactions representing the adsorption of dyes to the kaolinite face. Previous work (Harris *et al.*, 2006b) had shown that there was negligible interaction between Cd and dye. Parameters characteristic of the kaolinite surfaces (capacitances, site densities and equilibrium constants for protonation reactions) and equilibrium constants for Cd adsorption were introduced as fixed values. Equilibrium constants for dye adsorption reactions were then estimated from titration data for dye-kaolinite systems and dye adsorption data. The choice of surface species was constrained by results from ATR-FTIR measurements (Harris *et al.*, 2006a). Acid dissociation constants for the dyes were from a previous paper (Harris *et al.*, 2006a). During modeling of the ternary Cd-dye-mineral systems, all parameters previously determined for the various binary systems were held constant.

Because of the range of data available it was not feasible to automate the whole modeling process. Fitting of each system was done in an iterative manner, using each set of titration and adsorption data. Many different combinations of reactions consistent with the experimental data were tested. The reactions and parameters presented here represent a compromise giving the best fit for the different types of data.

## FORMULATION OF THE MODELS

### *General principles*

The surface complexation models were designed to follow the behavior observed in the experimental studies (Harris *et al.*, 2001, 2006a, 2006b), from which a number of qualitative deductions had previously been drawn:

*Dyes adsorb as outer-sphere complexes at the silica faces*. Adsorbed dye species are modeled as outer-sphere complexes at sites on the permanent negatively charged kaolinite surfaces.

*Dyes adsorb as aggregates*. Although the experimental data suggested that the dyes may adsorb as aggregates of six or seven molecules, we restricted the size of the aggregates to three or four molecules, which were the smallest that fitted the data reasonably closely. The use

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of much larger aggregates, with correspondingly larger charges, also tended to overload the optimization routines of the fitting software.

*Binding is partly electrostatic*. The adsorbed dye species are complexes between cationic dye aggregates and the permanent negatively charged silica surfaces of kaolinite. There is no adsorption under conditions in which the dye molecules carry no charge at all.

*Binding is partly hydrophobic*. Dye complexes are restricted to the silica face of kaolinite, which has hydrophobic character (Tunega *et al.*, 2004). The surface complexes that best fitted the data, particularly at low pH, are such that stabilization by electrostatic interaction alone is unlikely. This is discussed in more detail below.

### *Reactions*

The reactions utilized in the final models are listed in Table 1, together with the best-fitting values of the parameters. They are described in more detail in the following paragraphs.

*Kaolinite protonation*. Following Harris *et al.* (2006b), surface protonation of kaolinite was modeled by the reactions:

$$[X^-{-}H^+]^0 + K^+ \rightleftharpoons [X^-{-}K^+]^0 + H^+ \quad (1)$$

$$SOH \rightleftharpoons SO^- + H^+ \quad (2)$$

and

$$SOH_2^+ \rightleftharpoons SOH + H^+ \quad (3)$$

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.

*Adsorption of Cd*. Cd(II) adsorption was modeled (Harris *et al.*, 2006b) by two surface reactions:

$$Cd^{2+} + 2[X^-{-}K^+]^0 \rightleftharpoons [(X^-)_2{-}Cd^{2+}]^0 + 2K^+ \quad (4)$$

and

$$2SOH + Cd^{2+} \rightleftharpoons (SO)_2Cd + 2H^+ \quad (5)$$

Table 1. Surface complexation parameters for $Cd^{2+}$ and dye adsorption onto kaolinite.

| | | | | |
|---|---|---|---|---|
| $pK_w$ | | | 14.00[a] | |
| Formation constants ($log_{10}K$): | | | | |
| $CdOH^+$ | | | −10.08[b] | |
| $Cd(OH)_{2\ (aq)}$ | | | −20.36[b] | |
| Surface reactions ($log_{10}K$): | | | | |
| (1) $SOH + H^+ \rightleftharpoons SOH_2^+$ | | | 3.25[c] | |
| (2) $SOH \rightleftharpoons SO^- + H^+$ | | | −6.86[c] | |
| (3) $[X^-{-}H^+]^0 + K^+ \rightleftharpoons [X^-{-}K^+]^0 + H^+$ | | | −2.74[c] | |
| (4) $Cd^{2+} + 2[X^-{-}K^+]^0 \rightleftharpoons [2X^-{-}Cd^{2+}]^0 + 2K^+$ | | | 3.17[c] | |
| (5) $2SOH + Cd^{2+} \rightleftharpoons (SO)_2Cd + 2H^+$ | | | −7.67[c] | |
| Other parameters: | Ajax kaolinite | | Comalco kaolinite | |
| Site density $XH$ (μmol $m^{-2}$) | 2.0 | | 0.8 | |
| Site density SOH (μmol $m^{-2}$) | 3.2 | | 1.7 | |
| Specific capacitance, inner, $\kappa_1$ (F $m^{-2}$) | | 3.0 | | |
| Specific capacitance, outer, $\kappa_2$ (F $m^{-2}$) | | 7.0 | | |
| Reactions for Dyes ($log_{10}K$): | 9-Aa | 3,6-Daa | Az-A | Saf-O |
| (6) $DyeH^+ \rightleftharpoons Dye + H^+$ | −9.85 | −9.53 | | |
| (7) $DyeH^{2+} \rightleftharpoons Dye^+ + H^+$ | | | −10.6 | −11.2 |
| (8) $[[X^-{-}H^+]^0 + 3\ DyeH^+ \rightleftharpoons [X^-{-}Dye_3H_4^{4+}]^{3+}$ | 16.3 | 16.5 | | |
| (9) $[X^-{-}H^+]^0 + 3\ DyeH^+ \rightleftharpoons [X^-{-}Dye_3H_3^{3+}]^{2+} + H^+$ | 9.7 | 9.7 | | |
| (10) $[X^-{-}H^+]^0 + 3\ DyeH^+ \rightleftharpoons [X^-{-}Dye_3H^+]^0 + 3H^+$ | −10.1 | −9.7 | | |
| (11) $[X^-{-}H^+]^0 + 3\ DyeH^{2+} \rightleftharpoons [X^-{-}Dye_3H_4^{7+}]^{6+}$ | | | 18.5[d] | 16.5[d] |
| (12) $[X^-{-}H^+]^0 + 3\ DyeH^{2+} \rightleftharpoons [X^-{-}Dye_3H_3^{6+}]^{5+} + H^+$ | | | 12.5[d] | 9.5[d] |
| (13) $[X^-{-}H^+]^0 + 4\ DyeH^{2+} \rightleftharpoons [X^-{-}Dye_4H_2^{6+}]^{5+} + 3H^+$ | | | −5.0[d] | −8.5[d] |

[a] Lide and Frederikse (1994)
[b] Baes and Mesmer (1976)[c] Harris *et al.* (2006b)
[d] For these surface complexes, the charge in the β-plane is assumed to be less than the total charge on the dye aggregate: +4 for reaction 11, +3 for reaction 12, and +2 for reaction 13.

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

*Adsorption of dyes*. Slightly different reactions were required for the singly protonated aminoacridines (9-Aa and 3,6-Daa) and the doubly protonated dyes (Az-A and Saf-O). Deprotonation of 9-Aa and 3,6-Daa was represented as

$$DyeH^+ \rightleftharpoons Dye + H^+ \quad (6)$$

and deprotonation of Az-A and Saf-O by

$$DyeH^{2+} \rightleftharpoons Dye^+ + H^+ \quad (7)$$

The adsorption reactions for the aminoacridines were

$$[X^- - H^+]^0 + 3\ DyeH^+ \rightleftharpoons [X^- - Dye_3H_4^{4+}]^{3+} \quad (8)$$
$$[X^- - H^+]^0 + 3\ DyeH^+ \rightleftharpoons [X^- - Dye_3H_3^{3+}]^{2+} + H^+ \quad (9)$$

and

$$[X^- - H^+]^0 + 3\ DyeH^+ \rightleftharpoons [X^- - Dye_3H^+]^0 + 3H^+ \quad (10)$$

and those for Az-A and Saf-O were

$$[X^- - H^+]^0 + 3\ DyeH^{2+} \rightleftharpoons [X^- - Dye_3H_4^{7+}]^{6+} \quad (11)$$
$$[X^- - H^+]^0 + 3\ DyeH^{2+} \rightleftharpoons [X^- - Dye_3H_3^{6+}]^{5+} + H^+ \quad (12)$$

and

$$[X^- - H^+]^0 + 4\ DyeH^{2+} \rightleftharpoons [X^- - Dye_4H_2^{6+}]^{5+} + 3H^+ \quad (13)$$

Equations 8 and 11 represent the purely hydrophobic adsorption of aggregates of three dye molecules to the silica face of kaolinite: these are the dominant adsorption reactions at low pH. In reactions 9 and 12, which are dominant at around pH 6–10, the surface aggregates are partially deprotonated. Equations 10 and 13 represent adsorption of aggregates of three or four dye molecules, respectively, with further deprotonation, which occurs particularly at high pH.

As noted above, the models incorporate the smallest aggregate sizes that give reasonably close fits to the data, and a minimal set of adsorbed complexes. Reactions 8–13 therefore represent only some of the many possibilities. In reality it would be expected that the (larger) dye aggregates would become gradually deprotonated as the pH rises, giving a much larger array of surface species.

*Comments*

It is likely that singly charged dye molecules (such as the aminoacridines below their $pK_a$s) can be oriented with the charged group in the β-plane, but the twin charges of Az-A and Saf-O are almost certainly distributed across the molecules. It would be virtually impossible to arrange an aggregate in such a way that all the positive charge is in the β-plane. So while the adsorbing species for Az-A and Saf-O carry charges of +6 and +7, not all of this charge will be present in the β-plane. For the purpose of modeling the adsorption of these molecules the charge at the β-plane was taken as +4, +3 and +2 for equations 11 to 13, respectively, corresponding to the number of acidic protons in each adsorbing species.

An important aim of our modeling was to keep the models as simple as possible while adequately describing the data. The addition of more surface reactions could improve the fit of the models, and there are doubtless more reactions taking place than are allowed for, but such a course would be contrary to the goal of simplicity. Furthermore, the introduction of an excessive number of adjustable parameters increases the uncertainty in each of the equilibrium constants, and results in a model that is predominantly mathematically based, with limited chemical validity.

## TESTING THE MODELS

*Titration of dye–kaolinite systems*

Figure 1 shows the data for the titration of kaolinite in the presence of each of the four dyes. The solid line in each figure represents the ECCM for the kaolinite–dye system, whereas the broken line represents the predicted outcome if in the titration there were no interaction between the dye and the surface.

The combination of the models for titrations of kaolinite and dyes alone, with no interaction between them (*i.e.* Table 1, reactions 1–7), closely fitted the experimental data (Figure 1, broken lines). However, sorption data (Harris *et al.*, 2006a) clearly indicate that the dyes adsorb to kaolinite: therefore there must be interactions, but they must involve minimal uptake or release of protons. We note that the reactions in Table 1 are written in terms of formal components that are not necessarily the predominant species at the pH at which the reactions occur. Although the complete models do not fit the titration data as closely as the 'no interactions' versions, they still follow the data reasonably well, and, taken with the other data modeled below, are satisfactory compromises.

*pH dependence of adsorption*

Figures 2–5 show the speciation and fit of the ECC models to the data for dye adsorption as a function of pH. These figures include data for adsorption to both Ajax and Comalco kaolinites (Harris *et al.*, 2006a); the same models describe adsorption to both samples. The crystals of Comalco kaolinite have less than half the face-to-edge ratio of those in Ajax kaolinite, and hence the faces account for much less of their total surface area. This is of particular significance, as the models only allow for adsorption to permanent charges on the silica face of kaolinite ($X^-$). The fact that the models fit data for the two different kaolinite samples is strong evidence in their support.

The surface area available for adsorption is not sufficient to account for the amount of dye adsorbed, and

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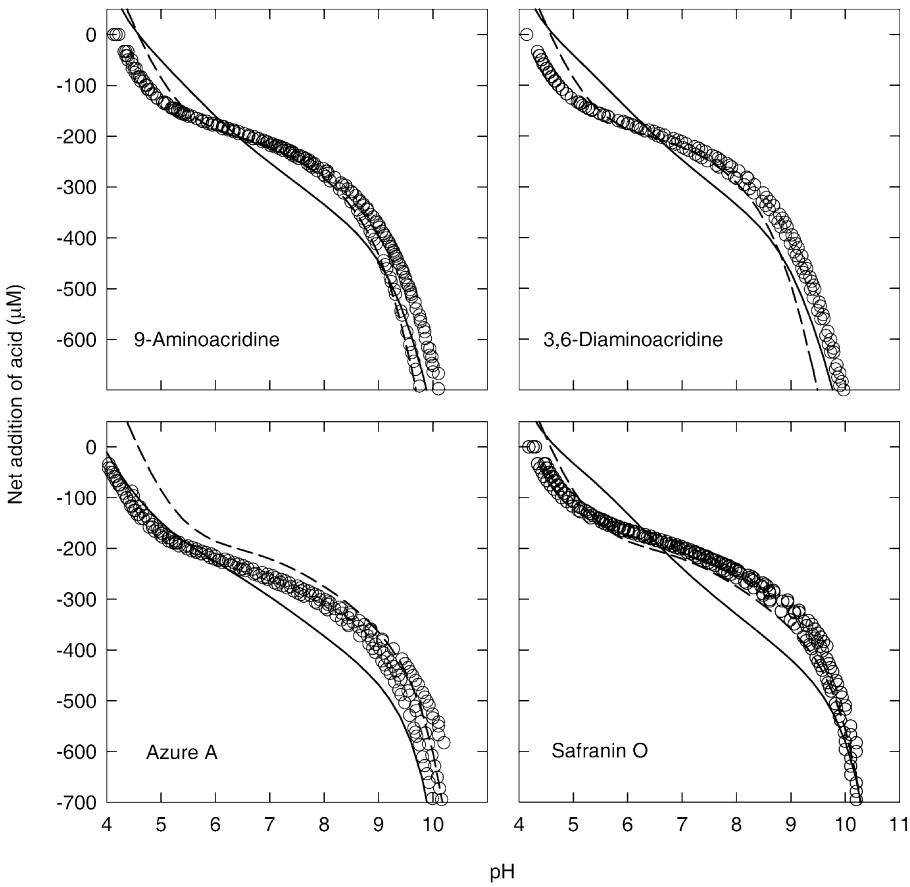


Figure 1. Titrations of Ajax kaolinite in the presence of dyes. The solid lines represent the complete models, with the parameters listed in Table 1. The broken lines represent a model system with no interactions between dye and kaolinite. [Kaolinite] = 100 $m^2L^{-1}$; [$KNO_3$] = 10 mM; [dye] = 600 μM.

hence the dyes cannot be adsorbing as a monolayer. Therefore the models allow for adsorption of dye trimers and tetramers. At low pH, the predominant adsorbed species are $[X^-\!-\!Dye_3H_4^{4+}]^{3+}$ for the two aminoacridines and $[X^-\!-\!Dye_3H_4^{7+}]^{6+}$ for Az-A and Saf-O. These species include one proton more than should strictly be allowed for: *e.g.* 9-Aa has a charge of +1, and hence a 9-Aa trimer should have a maximum charge of +3. A more realistic representation might be $[X^-\!-\!H^+,\ Dye_3H_3^{3+}]^{3+}$ for the aminoacridines or $[X^-\!-\!H^+,\ Dye_3H_3^{6+}]^{6+}$ for the other two dyes, indicating that the interaction between the silica face and the adsorbing species is largely hydrophobic with, perhaps, a contribution from hydrogen bonding. It was only by the inclusion of such species that adsorption at low pH could be modeled, especially in the case of the aminoacridine dyes.

At intermediate pH, the species $[X^-\!-\!Dye_3H_3^{3+}]^{2+}$ and $[X^-\!-\!Dye_3H_3^{6+}]^{5+}$ dominate for the acridines and Az-A and Saf-O, respectively. At high pH (>10 for the acridines and >11 for Az-A and Saf-O), the species $[X^-\!-\!Dye_3H^+]^0$ is dominant for the acridines and $[X^-\!-\!Dye_4H_2^{6+}]^{5+}$ for Az-A and Saf-O. Bonding for these species is probably through a combination of electrostatic and hydrophobic interactions.

*Dependence of adsorption on dye concentration (isotherms)*

As in previous studies (Angove *et al.*, 1998; Ikhsan *et al.*, 1999; Lackovic *et al.*, 2003b) it proved difficult to formulate surface complexation models that could fit isotherm data as well as those for titrations and pH-dependent adsorption. The isotherm experiments differed from the others (from which the models were developed) in several ways: the adsorbate concentrations changed throughout the experiments; the ratio of adsorbate to adsorbent covered a much broader range than in other experiments; the surfaces themselves changed during the experiments as more and more dye adsorbed. Finally, there may have been surface species important to the isotherm experiments that did not contribute significantly either to the titrations or the pH-dependent adsorption experiments (confined to relatively low dye concentrations) or to the spectroscopic measurements (at relatively high adsorbate concentrations), and hence were not included in the models.

Not surprisingly, then, it was difficult to find a single set of parameters to describe experiments with constantly changing conditions. In spite of this, the models developed from the titration and pH-dependent adsorp-

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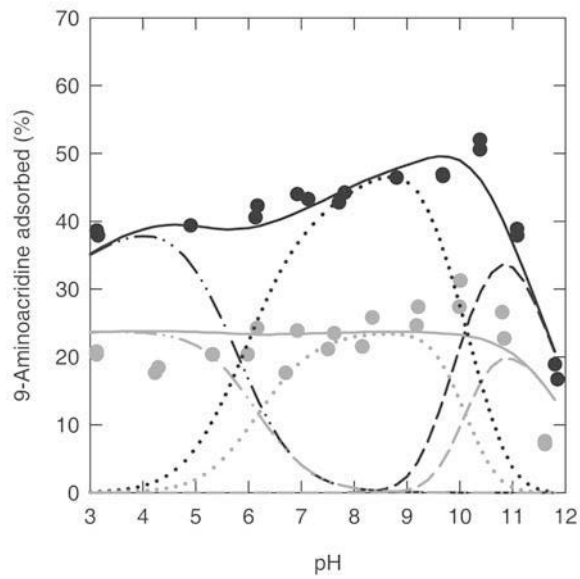


Figure 2. Speciation diagram for the adsorption of 9-Aa onto Ajax and Comalco kaolinites. Experimental data for Ajax kaolinite are represented by black symbols and fitted data by black lines. Those for Comalco kaolinite are in gray. Solid lines (——) represent the model, with the parameters in Table 1. Contributions from the different adsorbing species (complexes) are: (— ··) $[X^{-}\text{–}Dye_3H_4^{4+}]^{3+}$; (·····) $[X^{-}\text{–}Dye_3H_3^{3+}]^{2+}$; (– –) $[X^{-}\text{–}Dye_3H^{+}]^{0}$. [Ajax kaolinite] = 8 $m^2L^{-1}$; [Comalco kaolinite] = 8 $m^2L^{-1}$; [dye] = 80 μM (Ajax system) or 100 μM (Comalco system); [$KNO_3$] = 10 mM.

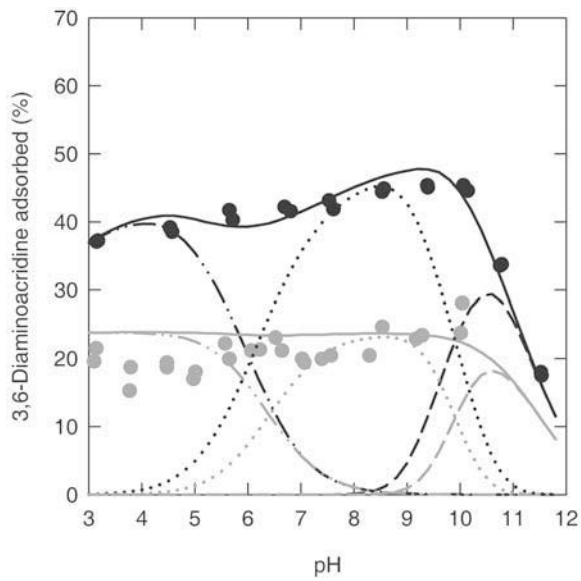


Figure 3. Speciation diagram for the adsorption of 3,6-Daa onto Ajax and Comalco kaolinites. Experimental data for Ajax kaolinite are represented by black symbols and fitted data by black lines. Those for Comalco kaolinite are in gray. Solid lines (——) represent the model, with the parameters in Table 1. Contributions from the different adsorbing species (complexes) are: (– ··) $[X^{-}\text{–}Dye_3H_4^{4+}]^{3+}$; (·····) $[X^{-}\text{–}Dye_3H_3^{3+}]^{2+}$; (– –) $[X^{-}\text{–}Dye_3H^{+}]^{0}$. [Ajax kaolinite] = 8 $m^2L^{-1}$; [Comalco kaolinite] = 8 $m^2L^{-1}$; [dye] = 80 μM (Ajax system) or 100 μM (Comalco system); [$KNO_3$] = 10 mM.

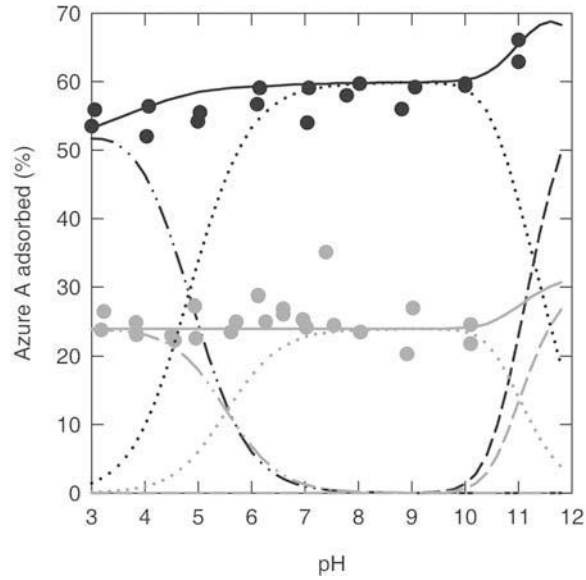


Figure 4. Speciation diagram for the adsorption of Az-A onto Ajax and Comalco kaolinites. Experimental data for Ajax kaolinite are represented by black symbols and fitted data by black lines. Those for Comalco kaolinite are in gray. Solid lines (——) represent the model, with the parameters in Table 1. Contributions from the different adsorbing species (complexes) are: (– ··) $[X^{-}\text{–}Dye_3H_4^{7+}]^{6+}$; (·····) $[X^{-}\text{–}Dye_3H_3^{6+}]^{5+}$; (– –) $[X^{-}\text{–}Dye_4H_2^{6+}]^{5+}$. [Ajax kaolinite] = 8 $m^2L^{-1}$; [Comalco kaolinite] = 8 $m^2L^{-1}$; [dye] = 80 μM (Ajax system) or 100 μM (Comalco system); [$KNO_3$] = 10 mM.

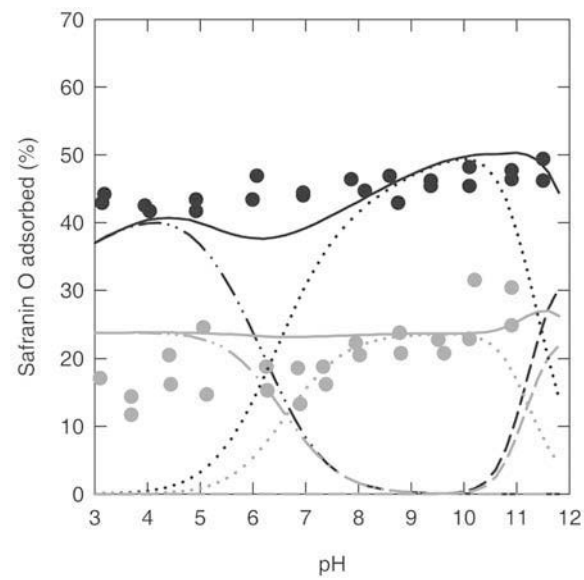


Figure 5. Speciation diagram for the adsorption of Saf-O onto Ajax and Comalco kaolinites. Experimental data for Ajax kaolinite are represented by black symbols and fitted data by black lines. Those for Comalco kaolinite are in gray. Solid lines (—) represent the model, with the parameters in Table 1. Contributions from the different adsorbing species (complexes) are: (– ··) $[X^{-}\text{–}Dye_3H_4^{7+}]^{6+}$, (·····) $[X^{-}\text{–}Dye_3H_3^{6+}]^{5+}$; (– –) $[X^{-}\text{–}Dye_4H_2^{6+}]^{5+}$. [Ajax kaolinite] = 8 $m^2L^{-1}$; [Comalco kaolinite] = 8 $m^2L^{-1}$; [dye] = 80 μM (Ajax system) or 100 μM (Comalco system); [$KNO_3$] = 10 mM.

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tion data also follow the trends of most of the constant-pH isotherm data (Figure 6).

The model for 9-Aa follows the isotherm data at both pH 5.5 and 9.0, although it underestimates the adsorption at pH 9.0 over the whole concentration range, and overestimates the adsorption at pH 5.5 at higher dye concentrations. For 3,6-Daa the model significantly underestimates adsorption at low dye concentrations, and overestimates it at higher concentrations. The apparent desorption at higher concentrations at pH 5.5 cannot be accommodated. The fitted lines for Az-A fit the data closely except at the highest concentrations. The close fit at low concentrations contrasts with the results for 3,6-Daa and Saf-O. The fit of the model for Saf-O is disappointing at low concentrations, where adsorption is substantially underestimated, but at pH 9.0 the fitted lines follow the data well at higher concentrations.

*Competitive adsorption of Cd and dyes*

In experiments on the competitive adsorption of Cd and dyes (Harris *et al.*, 2006b), Cd was used as a probe to determine the sites at which dyes adsorb. Previous experiments had shown that at low ionic strength, Cd adsorbs only to the faces of kaolinite at low pH, but as the pH increases it is progressively transferred to the crystal edges. Since dyes adsorb only to face sites, they compete with Cd for adsorption sites up to about pH 6, less so at higher pH, and not at all by about pH 9.

In the presence of dyes at relatively low concentration (100 μM), adsorption of $Cd^{2+}$ to the basal face of kaolinite is reduced (Harris *et al.*, 2006b), and at high dye concentration (where dye adsorption approaches saturation) it is almost totally suppressed. The ECC models (Figure 7) fit the data well for $Cd^{2+}$ adsorption in the presence of all of the dyes. No ternary (kaolinite-dye-Cd) complexes are required to model the data, suggesting that desorption of $Cd^{2+}$ is due to simple competition for sites on the silica face of kaolinite.

As was seen for the Langmuir models (Harris *et al.*, 2006b), the equilibrium constants for dye adsorption are much greater than those for Cd adsorption, which is again consistent with simple competition for surface sites between the two adsorbates.

*Displacement of Cd by dyes*

The ECC models also describe remarkably well the progressive desorption of Cd on the addition of 9-Aa or Az-A (Figure 8). The amount of Cd adsorbed at pH 7.5 was slightly underestimated over most of the range of dye concentration, and at pH 5.5 the models slightly underestimate the extent to which Cd is displaced on addition of the dyes, resulting in a slightly smaller slope for the desorption curve than is found experimentally. However, the general agreement with the experimental data supports the choice of trimers (and tetramers) for modeling adsorbed dye aggregates.

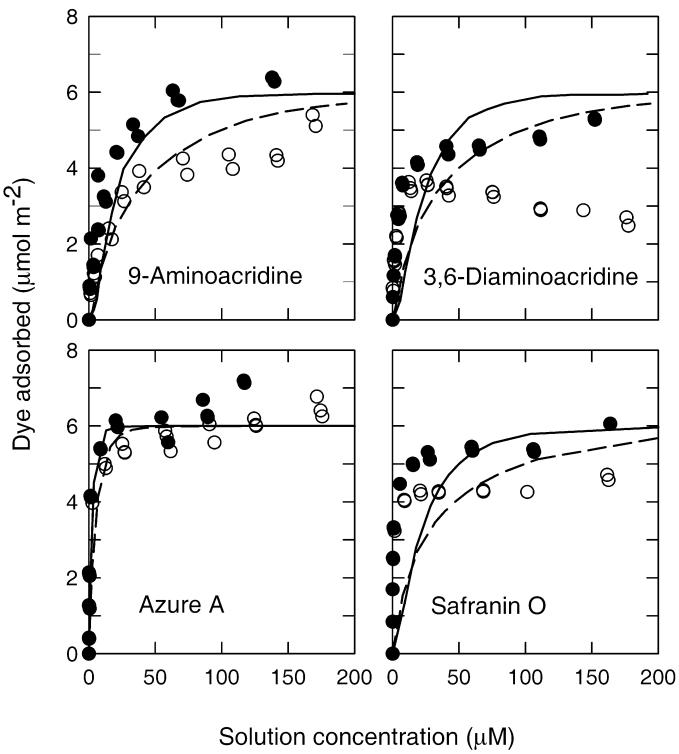


Figure 6. Adsorption isotherms for Ajax kaolinite. Open circles are experimental data for pH 5.5, and filled circles for pH 9.0. Lines represent the ECCMs (parameters in Table 1): (– –) pH 5.5; (—) pH 9.0. [Kaolinite] = 8 $m^2L^{-1}$; [$KNO_3$] = 10 mM.

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## DISCUSSION

The principal challenge for this study was to construct models that described the data adequately and at the same time were chemically reasonable. The outcome was necessarily a compromise, and there are certainly other approaches that might have been followed. For example, if our models are modified by eliminating electrostatic interactions between dye and surface, all sets of data fit better except the isotherms, which suffer considerably. However, ignoring electrostatic interactions is difficult to justify, and models that describe all of the data fairly well were deemed superior to those describing only some of the data, albeit very well. Similarly, dye aggregates of variable size, or even a distribution of aggregates, might have been chosen, but at the expense of simplicity.

Another limitation is that ECCMs assume that adsorbates are point charges, which is not the case for dye molecules. Although we could have pursued more complex models that allowed explicitly for a distribution of charge in the adsorbed layers, we preferred to retain the simplicity of the ECCMs, making only a slight adjustment to the effective charges of some of the dye aggregates to accommodate this deficiency.

The inclusion of more surface complexes would allow closer fitting to the data. The problem with that approach is that the introduction of more variables quickly leads to a situation where the models become little more than curve-fitting devices, even if they might appear to be chemically realistic. Our results show that it is possible to develop simple quantitative models with a minimum of chemical species that are consistent with a range of experimental data including those for ternary dye-Cd-kaolinite systems.

The ECC models described here are consistent with the spectroscopic and quantitative adsorption data, and require relatively small numbers of adjustable parameters, of which only a small number were permitted to vary at any stage of the modeling. They describe diverse sets of experimental data sufficiently well to give confidence to the broad nature of the hypotheses on which they are based.

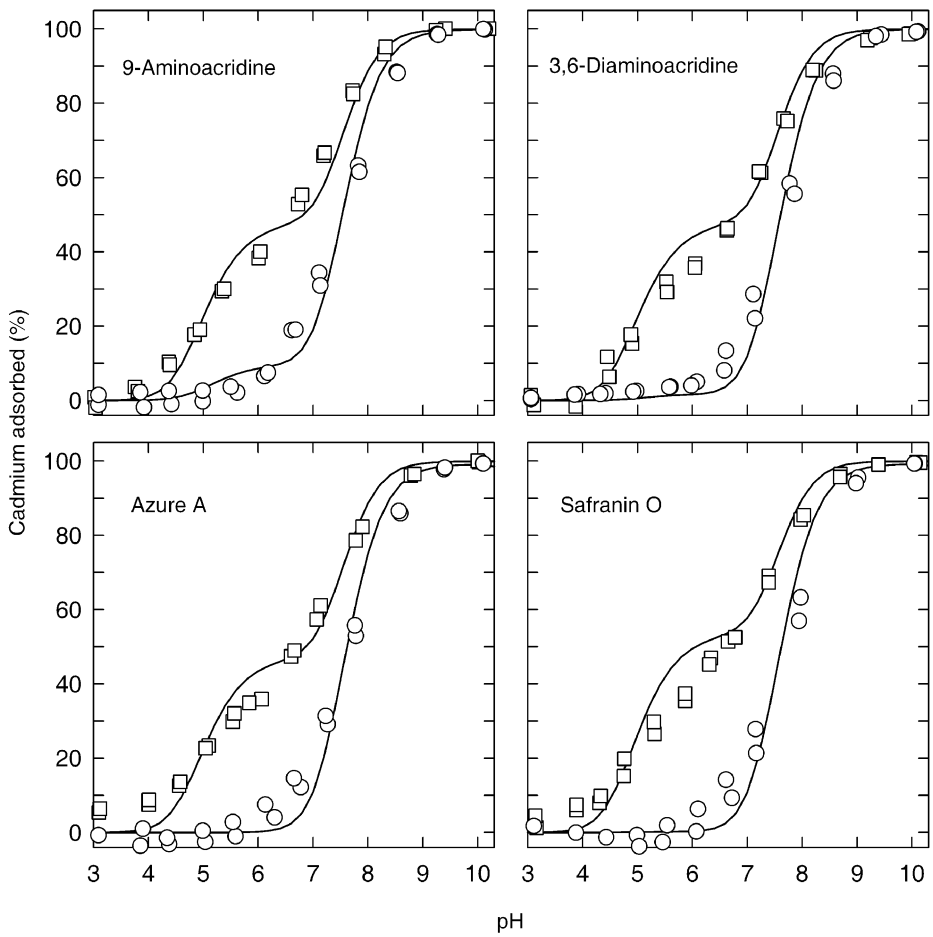


Figure 7. Adsorption of $Cd^{2+}$ in the presence of dyes: (□) [dye] = 100 μM; (○) [dye] = 500 μM 9-Aa; 650 μM 3,6-Daa; 700 μM Az-A; or 900 μM Saf-O). The lines represent the total adsorbed Cd, predicted by the ECCMs. [Kaolinite] = 100 $m^2L^{-1}$; [$Cd^{2+}$] = 50 μM; [$KNO_3$] = 5 mM.

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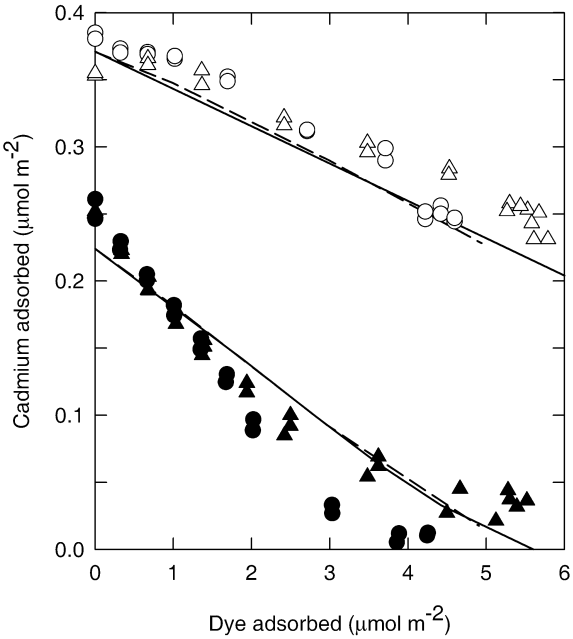


Figure 8. Displacement of Cd (50 μM) from kaolinite by (○) 9-aminoacridine and (△) azure A, at pH 5.5 (filled symbols) and 7.5 (open symbols). The lines are those predicted by the ECCM (parameters in Table 1) for (—) 9-Aa and (– –) Az-A. [Kaolinite] = 100 $m^2L^{-1}$; [$Cd^{2+}$] = 50 μM; [$KNO_3$] = 5 mM; [dye] = 0–700 μM.

## CONCLUSIONS

Simple extended constant capacitance surface complexation models describe the adsorption of the four dyes 9-aminoacridine, 3,6-diaminoacridine, azure A and safranin O to kaolinite, and the competitive adsorption of the dyes with Cd. The generally satisfactory fitting of the models to a wide range of experimental data supports the view that the dyes adsorb only to the somewhat hydrophobic but anionic silica faces of kaolinite, which act as a template for the aggregation of dye molecules, leading to multilayer adsorption. Although the adsorption is largely hydrophobic in nature, a degree of electrostatic attraction is necessary to stabilize the adsorption of the dyes.

## REFERENCES

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.

Baes, C.F.J. and Mesmer, R.E. (1976) *The Hydrolysis of Cations*. John Wiley & Sons, New York.

Davis, J.A., James, R.O. and Leckie, J.O. (1978) Surface ionization and complexation at the oxide/water interface. I. Computation of electrical double layer properties in simple electrolytes. *Journal of Colloid and Interface Science*, **63**, 480–499.

De, D.K., Chakravarti, S.K. and Mukherjee, S.K. (1967) Studies on the sorption and desorption of methylene blue on kaolinite. *Journal of the Indian Chemical Society*, **44**, 743–746.

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., Wells, J.D. and Johnson, B.B. (2006b) Competitive adsorption of Cd and dyes to kaolinite. *Clays and Clay Minerals*, **54**, 449–455.

Ikhsan, J., Johnson, B.B. and Wells, J.D. (1999) A comparative study of the adsorption of transition metals on kaolinite. *Journal of Colloid and Interface Science*, **217**, 403–410.

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.

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.

Nir, S. (1984) A model for cation adsorption in closed systems: Application to calcium binding to phospholipid vesicles. *Journal of Colloid and Interface Science*, **102**, 313–321.

Nir, S., Rytwo, G., Yermiyahu, U. and Margulies, L. (1994) A model for cation adsorption to clays and membranes. *Colloid and Polymer Science*, **272**, 619–632.

Nir, S., Undabeytia, T., Yaron-Marcovich, D., El-Nahhal, Y., Polubesova, T., Serban, C., Rytwo, G., Lagaly, G. and Rubin, B. (2000) Optimization of adsorption of hydrophobic herbicides on montmorillonite preadsorbed by monovalent organic cations: Interaction between phenyl rings. *Environmental Science and Technology*, **34**, 1269–1274.

Nordin, J., Persson, P., Nordin, A. and Sjöberg, S. (1998) Inner-sphere and outer-sphere complexation of a polycarboxylic acid at the water-boehmite (γ-AlOOH) interface: A combined potentiometric and IR spectroscopic study. *Langmuir*, **14**, 3655–3662.

Persson, P., Nordin, J., Rosenqvist, J., Lövgren, L., Öhman, L.-O. and Sjöberg, S. (1998) Comparison of the adsorption of *o*-phthalate on boehmite (γ-AlOOH), aged γ-$Al_2O_3$, and goethite (α-FeOOH). *Journal of Colloid and Interface Science*, **206**, 252–266.

Polubesova, T. and Nir, S. (1999) Modeling of organic and inorganic cation sorption by illite. *Clays and Clay Minerals*, **47**, 366–374.

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.

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., Nir, S., Margulies, L., Casal, B., Merino, J., Ruiz-

https://doi.org/10.1346/CCMN.2006.0540406 Published online by Cambridge University Press

Hitzky, E. and Serratosa, J.M. (1998) Adsorption of monovalent organic cations on sepiolite: Experimental results and model calculations. *Clays and Clay Minerals*, **46**, 340–348.

Tunega, D., Gerzabek, M.H. and Lischka, H. (2004) Ab initio molecular dynamics study of a monomolecular water layer on octahedral and tetrahedral kaolinite surfaces. *Journal of Physical Chemistry B*, **108**, 5930–5936.

Venema, P., Hiemstra, T. and van Riemsdijk, W.H. (1996) Multisite adsorption of cadmium on goethite. *Journal of Colloid and Interface Science*, **183**, 515–527.

Venkata Rao, B. and Sastry, C.A. (1987) Removal of dyes from water and wastewater by adsorption. *Indian Journal of Environmental Protection*, **7**, 363–373.

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https://doi.org/10.1346/CCMN.2006.0540406 Published online by Cambridge University Press