

ROLE OF IRON OXIDES IN THE PHOSPHATE ADSORPTION PROPERTIES OF KAOLINITES FROM THE IVORY COAST

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Abstract—The phosphate adsorption properties of three clay samples, with kaolinite as the dominant mineral, from different deposits in the Ivory Coast have been investigated. The clays contain varying amounts of crystalline Fe oxides and kaolinite with structural Fe. All measurements were made in dilute suspension under controlled conditions of temperature, pH, ionic strength and saturating cation. Data have been fitted to Langmuir adsorption isotherms. Both P adsorption and surface area measurements have been made on samples before and after chemical removal of Fe oxides. The samples have large P adsorption capacities, which are not entirely explained by their large specific surface areas. The presence of Fe oxides makes a strong contribution to the surface area and enhances the adsorption capacities. There is little evidence that structural Fe makes a strong contribution to the enhanced P adsorption capacity.

Key Words—Adsorption, Fe Oxide, Goethite, Hematite, Kaolinite, Langmuir, Phosphate.

INTRODUCTION

There are considerable mineral deposits in the Ivory Coast and to date they have been largely unexploited. Preliminary field studies and mineralogical analyses confirm that the major mineral present is kaolinite, as would be expected in tropical climates. However the clays are often highly colored, indicating the presence of Fe oxides. This study is part of a comprehensive investigation of the structure and properties of some of these clays. The broad aim is to characterize the minerals and to test their suitability for various applications.

A well known feature of kaolinites is their large capacity to adsorb phosphate and other oxyanions, such as arsenate. This contributes to their role in soil fertility, but also suggests the possible use in remediation. The present study concentrates on the phosphate adsorption properties of three mineral samples. The effects of charge-compensating cations, ionic strength and pH have been measured. Adsorption isotherms, fitted to the linearized Langmuir isotherm, have been obtained with and without removal of Fe oxides.

Our aim is to compare these properties with those of reference kaolinites, and to explain the differences. Kaolinites from soil and some natural deposits have larger surface area, are less crystalline and have a greater anion adsorption capacity than reference samples (Singh and Gilkes, 1992). Because these differences are often

ascribed to the presence of Fe oxides, we have concentrated on the role of such impurities. We have attempted to elucidate the nature of the interaction between the oxides and the clay mineral by comparing adsorption with and without removal of Fe oxides. If the dissolved minerals were present as coatings they could be expected to have dominated the adsorption properties whereas the treated material would have characteristic kaolinite properties. Conversely, if the initial material were a mixture of two independent components, with little interaction, then the adsorption properties would be a weighted average of those of each component. We have also tried to assess to what extent the known influence of impurities on crystal size and ordering affects the adsorption properties.

MATERIALS AND METHODS

Clays were sampled from three deposits in the Ivory Coast. The following abbreviations are used: Adatié

Table 1. Some properties of the clay minerals.

	GB	NS	ADA
Elemental analysis (g kg ⁻¹)			
SiO ₂	533	516	514
Al ₂ O ₃	236	313	312
Fe ₂ O ₃	97	35	38
TiO ₂	16	23	6
K ₂ O	15	3	31
MgO	3	0	0
H ₂ O	95	111	100
Fe oxide detected by			
Mössbauer spectroscopy	goethite	hematite	—
Other impurities			
	illite	illite	illite
	quartz	quartz	quartz
	lepidocrocite	anatase	

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(ADA), Grand-Bassam (GB) and Nigui-Saff (NS). The clay-sized fraction ($<2 \mu\text{m}$) was obtained by sedimentation. Table 1 shows the elemental analysis of the clays obtained by X-ray fluorescence (XRF) and the major impurities detected by Mössbauer spectroscopy and X-ray diffraction. Neither organic carbon nor Mn oxides were detected. The clays differ in their color, suggesting the presence of Fe oxides in addition to structural Fe, which was confirmed by Mössbauer spectroscopy (see Table 1) – GB clay has a yellowish ochre color, the NS is a dull rust whereas the ADA is white. More detail of the mineralogical and structural analysis of these and related clay samples is given by Sei (1998). Part of each clay-sized fraction was treated with dithionite-citrate-bicarbonate (DCB) to remove Fe oxides (Mehra and Jackson, 1960). The goethite and hematite features of the Mössbauer spectra of GB and NS disappeared after the DCB treatment (not shown). The Fe thus removed was analyzed colorimetrically. Both the untreated and DCB-samples were then made homo-ionic in either Na or Mg by three washings in 1 M chloride solutions followed by washing in deionized water until salt-free. The clays were stored at 4°C as salt-free suspensions until required. The specific surface area of each sample was measured by the N_2 -BET method. Mössbauer spectra were recorded in standard transmission geometry in constant acceleration mode at 300 K and 80 K (in a liquid nitrogen flow cryostat) using a ^{57}Co source in a Rh matrix. X-ray diffraction (XRD) performed with a Philips diffractometer using $\text{CuK}\alpha$ radiation, showed that the dominant phase in all samples is kaolinite, along with quartz and illite impurities. Small amounts of feldspar were detected in ADA and GB. Goethite and lepidocrocite were identified in GB and anatase in NS.

Phosphate adsorption was measured in dilute suspension (10 g dm^{-3}) at $20 \pm 0.5^\circ\text{C}$ and controlled ionic strength. Triplicate suspensions were prepared by pipetting clay suspension into a 0.01 M (unless otherwise stated) solution of the chloride salt of the charge compensating cation (Na or Mg) with differing concentrations of phosphate (0 – 10^{-3} M). No adjustment of pH was made, except in the study of pH effect when either HCl or NaOH was added to the initial phosphate + electrolyte solution. The suspensions were shaken for 48 h, then centrifuged (30 min at 40,000 g). Preliminary trials showed that no further adsorption was detected after 24 h. The phosphate concentration in the supernatant solution was measured using the molybdate blue method (Murphy and Riley, 1962) and the amount adsorbed calculated by comparison with the initial solution concentrations. The data are presented either in graphic form as adsorbed concentration, x_{ads} , as a function of final solution concentration, $[P]$, or the Langmuir parameters, maximum adsorbed concentration (x_{max}) and affinity parameter (K) given in Table 2. The Langmuir parameters were obtained from linear regressions of the linear form of that isotherm, written as

$$\frac{[P]}{x_{\text{ads}}} = \frac{1}{Kx_{\text{max}}} + \frac{[P]}{x_{\text{max}}} \quad (1)$$

For studies of the effects of pH and of ionic strength, a single initial phosphate concentration was used (2.5×10^{-4} M).

RESULTS

Figure 1 shows the adsorption of phosphate on each of the three clays, with either Na or Mg as the charge-compensating cation, as a function of final solution phase phosphate concentration. For each sample, adsorption increases to a maximum. Although the Langmuir, Freundlich and Temkin adsorption isotherms all gave good fits to the data, the Langmuir model was preferred for ease of comparison with other published results. The fitted parameters are given in Table 2. The adsorption maxima (x_{max}) and to a lesser extent, the affinity parameters (K), decrease in the order $\text{GB} > \text{NS} > \text{ADA}$. Both the adsorption capacity and affinity are larger for the Mg-clays than the Na-samples, but the effect is smaller than the difference between clays.

Table 2 also shows the effect of DCB treatment on the Langmuir parameters of each clay, homo-ionic in either Na or Mg (insufficient material was available for Na ADA-DCB). Iron oxide removal decreases phosphate adsorption. The effect is greater than that of charge-compensating cation, but smaller than the difference between samples. Considerable differences in phosphate adsorption capacity between minerals remain even after the DCB treatment. The sextuplet peaks attributed to goethite and hematite in the GB and NS clays in the Mössbauer spectra (Sei, 1998) disappeared after this treatment, and the specific surface area decreased (Table 3). Figure 2 shows the phosphate adsorption capacity as a function of specific surface area for each

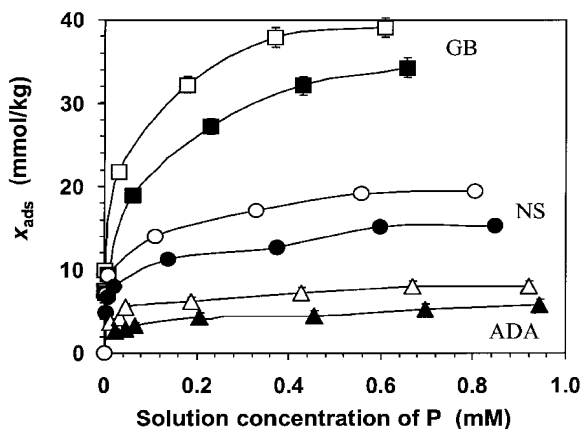


Figure 1. Effect of charge-compensating cation on phosphate adsorption by each clay fraction. The open symbols represent Mg-, and the closed symbols, Na-saturated minerals.

Table 2. Phosphate adsorption Langmuir parameters on each of the clay samples.

Saturating cation	Sample	x_{\max} (mmol kg ⁻¹)	$K \times 10^4$ (dm ³ mol ⁻¹)	R^2
Mg ²⁺	GB	39.6 ± 1.2	6.3 ± 0.9	0.998
	NS	19.9 ± 0.3	4.0 ± 0.8	0.998
	ADA	8.2 ± 0.5	3.0 ± 0.2	0.999
	GB-DCB	16.3 ± 0.2	2.2 ± 0.2	0.997
	NS-DCB	8.1 ± 0.5	1.7 ± 0.1	0.989
	ADA-DCB	1.4 ± 0.1	18.7 ± 1.1	0.999
Na ⁺	GB	35 ± 0.9	2.9 ± 0.8	0.997
	NS	15.5 ± 0.2	3.7 ± 0.5	0.996
	ADA	5.8 ± 0.3	1.7 ± 0.0	0.994
	GB-DCB	10.3 ± 0.1	0.3 ± 0.0	0.991
	NS-DCB	6.7 ± 0.3	1.4 ± 0.04	0.995

of the Mg-clays, before and after oxide extraction. Table 3 also gives the amount of Fe and Al removed by DCB. A preliminary trial showed that the possible presence of citrate remaining after the DCB treatment did not interfere with subsequent phosphate adsorption (data not shown).

Figure 3 shows the pH dependence of phosphate adsorption (initial [P] = 2.5×10^{-4} M) on the Na-clays before and after oxide removal for GB, NS and ADA (untreated sample only). Each sample shows a broad plateau where adsorption is independent of pH, with a decrease in adsorption when pH is increased beyond a threshold value of ~6.5. Only NS, before DCB treatment, also exhibits a decrease in adsorption at acid pH (below 4). Iron oxide removal decreases adsorption at all pH, particularly in the plateau region. The pH dependence of the Mg-clays (not shown) was very similar.

DISCUSSION

Adsorption on untreated clays

Although XRD analysis (Sei, 1998) shows that the major component of these samples is kaolinite, their phosphate adsorption properties differ from those of reference kaolinites. The phosphate adsorption capacity of each of the clays is larger than usually observed for reference kaolinites. For example, Singh and Gilkes (1992) found a value of $x_{\max} = 2.9 \times 10^{-3}$ mol kg⁻¹ (89 µg P g⁻¹) for Georgia kaolinite. The x_{\max} of these samples were 3–10 times larger, although that of ADA

was similar to the value reported by Kuo and Lotse (1972) for Ca-kaolinite. The greater adsorption capacity may be due in part to the specific surface area (33–63 m² g⁻¹) which is closer to that of soils (7–146 m² g⁻¹, average 30 m² g⁻¹, Borggaard, 1982), kaolinitic soil clays (~50 m² g⁻¹, Singh and Gilkes, 1992) or Fe oxides (8–348 m² g⁻¹, the largest values being for amorphous oxides, Borggaard, 1983a; Torrent *et al.*, 1990) than reference kaolinite (10 m² g⁻¹ for Georgia kaolinite; Singh and Gilkes, 1992). However, even when expressed with respect to surface area, the P adsorption (0.2–0.6 µmol m⁻²) is still larger than expected for kaolinite (0.12 µmol m⁻², Singh and Gilkes, 1992) and kaolinitic soil clays (0.35 µmol m⁻², Singh and Gilkes, 1992), but less than the theoretical value of Fe oxides (2.5 µmol m⁻², Torrent, 1997).

The pH dependence of P adsorption is much less than usually reported or predicted on kaolinite for phosphate or similar anions (such as arsenate). The constant capacitance and other models of adsorption of oxyanions on kaolinite and other variable-charge surfaces predict an adsorption maximum (Goldberg and Sposito, 1984; Manning and Goldberg, 1996). This is usually confirmed

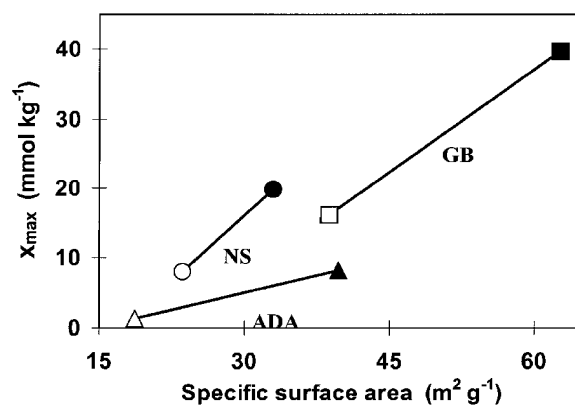


Figure 2. Phosphate adsorption maximum (x_{\max}) as a function of BET specific surface area, before (open symbols) and after (closed symbols) DCB treatment.

Table 3. Effect of DCB treatment on Mg-saturated clays.

	GB	NS	ADA
Specific surface area (m ² g ⁻¹)			
Before treatment	62.54	33.0	39.75
After treatment	38.76	23.63	18.71
Fe removed (g Fe kg ⁻¹)	29.24	11.49	0.24
% of Fe initially present	86	94	2
Al removed (g Al kg ⁻¹)	3.8	0.5	0.2
% of Al initially present	6.1	0.6	0.1

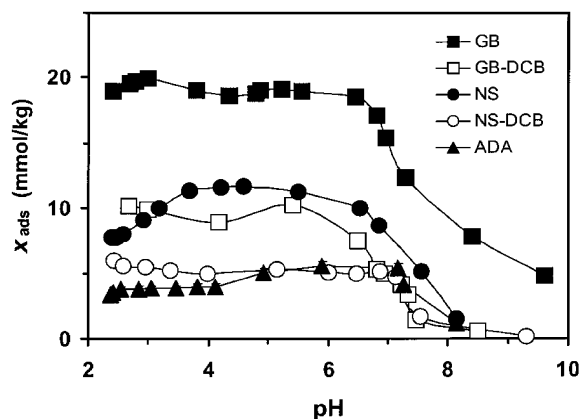


Figure 3. pH dependence of phosphate adsorption on each Na-saturated clay mineral before and after Fe oxide removal (ADA before treatment only).

by experimental data (Parfitt, 1978; White, 1980; Manning and Goldberg, 1996), although Bar-Yosef *et al.* (1988) also reported little pH dependence from pH 5 to >7. In contrast, only NS shows a clear, but broad, adsorption maximum, as is often the case for soils (Barrow, 1984). Moreover, the pH dependence is not similar to that of Fe oxides for which phosphate adsorption is always found to decrease with increasing pH in the range studied here, because of the high point of zero charge (pzc) (8–9). However, it should be noted that both experimental results and theory based on electrostatic interactions and surface complexation indicate that the pH dependence of phosphate adsorption on goethite decreases with decreasing P loading (Geelhoed *et al.*, 1997). Adsorption properties do not appear to be the weighted average of those of Fe oxides and kaolinites as would be expected for a simple mixture.

The effect of the charge-compensating cation is smaller than often reported (Parfitt, 1978; Pardo *et al.*, 1992; Carreira and Lajtha, 1997). Furthermore, the lesser adsorption in the presence of the mono-valent cation is a function of electrolyte concentration, or ionic strength. The cation effect decreases with increasing ionic strength for GB and ADA, but is constant for NS for salt concentrations between 1 mM and 0.3 M (Figure 4). The greater adsorption in the presence of divalent rather than mono-valent cations is usually attributed to the specific adsorption of divalent cations, thereby increasing surface positive charge, and the possibility of formation of bridging complexes. The relatively small effect of cations indicates that adsorption is mostly highly specific, as would be expected for kaolinite. The small cation effect may also reflect the conclusion of Ryden and Syers (1975) that the cation effect is largely kinetic in origin, since a rather long adsorption period was used.

Various features of the phosphate adsorption properties of these clay samples resemble those of soil kaolinites (Singh and Gilkes, 1992) or soils (Borggaard, 1983b; Pardo *et al.*, 1992; Yuan and

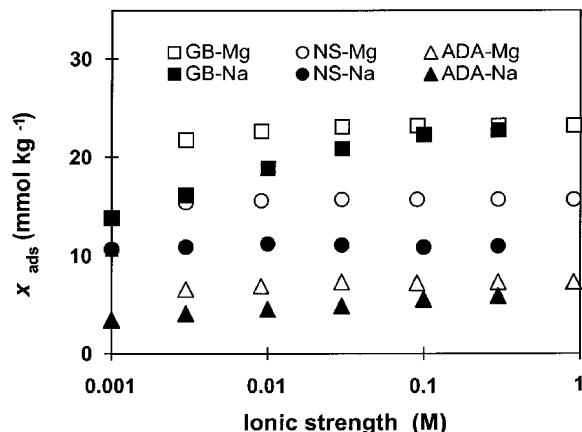


Figure 4. Effect of ionic strength on phosphate adsorption on each clay mineral.

Lavkulich, 1994), containing various mineral oxides and organic matter. No evidence of organic matter was found in these samples, therefore the differences from reference kaolinites may be attributed to the presence of inorganic impurities, particularly Fe oxides. There is much evidence to suggest that the phosphate adsorption capacity of soils and soil clays is strongly related to Fe oxide content (Borggaard, 1983b; Singh and Gilkes, 1992; Yuan and Lavkulich, 1994; Peña and Torrent, 1984). The reasons may be both direct and indirect. First, Fe oxides have a strong affinity for phosphate, as has been reviewed by Cornell and Schwertmann (1996) and Torrent (1997). Second, both the particle size, and therefore specific surface area, and the crystallinity of kaolinites may be related to the metal oxide content and the presence of structural Fe (Herbillon *et al.*, 1976; Mestdagh *et al.*, 1980; Singh and Gilkes, 1992; Sei, 1998). The former direct effect should disappear when the oxides are removed from the clay sample. However, the indirect effect of the presence of Fe oxides in the initial samples will persist on the clean clay mineral.

Properties of DCB-treated clays

The specific surface area of each of the clay samples is considerably decreased by the DCB treatment, even the ADA sample in which only structural Fe was detected by Mössbauer spectroscopy and from which little Fe was removed. The specific surface areas of treated NS and ADA are typical of reference kaolinites ($\sim 20 \text{ m}^2 \text{ g}^{-1}$), but that of GB remains larger. Minerals dissolved by DCB apparently contributed nearly half of the surface area of the original samples (28–53%). The small amount of Al dissolved suggests that the treatment does not appreciably solubilize kaolinite or Al oxides. The apparent surface area of Fe oxides may be estimated from the loss of surface area, relative to amount of Fe oxide removed, assuming that only goethite is present in GB and only hematite in NS. This gives the very large value of $\sim 500 \text{ m}^2 \text{ g}^{-1}$ for both minerals. For comparison,

Cornell and Schwertmann (1996) cite ranges of surface area of $8\text{--}200\text{ m}^2\text{ g}^{-1}$ for goethite and $2\text{--}90\text{ m}^2\text{ g}^{-1}$ for hematite, and Borggaard (1983a) reports $350\text{ m}^2\text{ g}^{-1}$ for amorphous oxides. This strongly suggests that Fe oxides are present either as amorphous oxides, which does not accord with the Mössbauer analysis or as very small crystals and probably as coatings. This explanation is impossible for ADA, since no Fe oxides were detected and almost no Fe removed by DCB. Neither can the loss of surface area be due to the removal of Al oxides, since little Al is removed by the DCB treatment. If the oxides were present as coatings and cementing agents between small mineral particles, their removal would reveal new kaolinite surfaces and so they would in fact account for an even greater proportion of the original surface. Furthermore, the removal of cementing agents would yield smaller kaolinite particles and so cause an increase in specific surface area.

Adsorption on DCB-treated clays

Phosphate adsorption properties are also modified by the DCB treatment. Adsorption is always smaller on treated samples, whatever the initial conditions (phosphate concentration, cation and pH). The decrease is not due simply to the smaller surface area, since the adsorption maximum is decreased whether the maximum adsorbed is expressed with respect to mass of solid x_{max} or surface area Q_{max} (Figure 5). The P adsorption capacities of the clean GB and NS clays, both with respect to mineral weight and surface area, are greater than that of reference kaolinite (3 mmol kg^{-1} or 0.12 mmol m^2 , Singh and Gilkes, 1992). This suggests that long-term weathering effects have modified the surface adsorption properties. The fact that the clean ADA sample has a lower P adsorption capacity than reference Georgia kaolinite, despite its structural Fe content, suggests that enhanced adsorption capacity is not due to structural Fe as suggested by Singh and Gilkes (1992).

Clearly, not only did the oxides contribute to surface area, but they also adsorbed phosphate more strongly than the clean kaolinite surface, as would be expected of Fe oxides. The decrease in adsorption capacity is greatest for ADA, which contained no Fe oxides, and lost only a very small amount of Al (in the form of oxides or dissolved kaolinite). Cabrera *et al.* (1977) showed that Al oxides have a greater affinity for phosphate than do Fe oxides, with respect to surface area. However they have smaller specific surface areas than do Fe oxides, so the large decrease in surface area of ADA is surprising. If we consider as above, that to a first approximation, the DCB treatment removes only goethite and hematite from samples GB and NS respectively, the P sorption capacity of both minerals can be calculated. In this way we find that the P sorption capacity of the GB goethite is 0.5 mol kg^{-1} (or 0.9 mol m^{-2}) and that of the NS hematite is 0.7 mol kg^{-1} (or 1.2 mol m^{-2}). Using a similar method, Singh and Gilkes (1992) calculated a P adsorption capacity for Fe oxides present in kaolinite soils about 2 to 3 times lower (8 g kg^{-1} or 0.26 mol kg^{-1}).

There is some change in the pH dependence of adsorption after the removal of oxides. For goethite-containing GB, the difference in x_{ads} with and without DCB treatment is constant throughout the pH range studied. The difference is smaller and the trend is slightly different for NB. For most of the pH range, x_{ads} is constant on the treated sample, only falling off above pH 7. The difference in phosphate adsorption is thus strongly pH dependent, absent at pH 2.5, increasing to a maximum around pH 5, and decreasing again towards alkaline pH. However the pH dependence of the treated samples does not resemble that of reference kaolinite. The clean mineral surface has been altered by the presence of the oxides. The untreated minerals would act as mixtures of kaolinite and Fe oxide and kaolinite, possibly dominated by Fe oxide, if the latter was present as a coating.

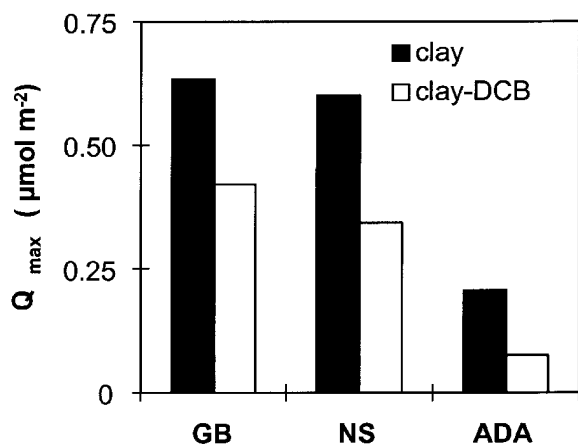


Figure 5. Phosphate adsorption maximum with respect to BET surface area before and after DCB treatment on each Mg-saturated sample.

CONCLUSIONS

Iron oxides play an important role in the phosphate adsorption capacity of these natural kaolinite samples. The pH dependence of the adsorption properties is not typical of either kaolinites or Fe oxides. Even after oxide removal, both the surface area and the adsorption capacity are greater than usually reported for kaolinites. The large surface area and the presence of both crystalline and poorly crystallized Fe oxides all contribute to the large phosphate adsorption capacity of these clays.

ACKNOWLEDGMENTS

The authors thank I. Bertrand and L. Roger for their assistance and advice and J. Torrent and J. Amonette for their critical comments on the first version of the script.

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(Received 14 June 1999; revised 25 September 2001; Ms. 351)