INTERACTIONS OF PHOSPHATES AND SELECTED ORGANIC MOLECULES WITH PALLYGORSKITE AND SEPIOLITE

A Thesis Submitted to the College of Graduate Studies and Research in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in the Department of Soil Science University of Saskatchewan

by

Hossein Shariatmadari
Saskatoon, Saskatchewan, Canada
Fall, 1998

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UNIVERSITY OF SASKATCHEWAN
College of Graduate Studies and Research

SUMMARY OF DISSERTATION
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of the requirements for the

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by
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Fall, 1998

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INTERACTIONS OF PHOSPHATES AND SELECTED ORGANIC MOLECULES WITH PALLYGORSKITE AND SEPIOLITE

Pallygorskite and sepiolite are silicate clay minerals that commonly occur in soils of arid and semiarid regions. Despite the significance of these minerals in soil agrochemistry and in a variety of industrial applications, the sorptive behavior of palygorskite and sepiolite is not fully elaborated. The objectives of this work were to: i) study the interactions of orthophosphate (Pi) and inositol hexaphosphate (IHP) with palygorskite and sepiolite in pure systems and in the presence of calcite and ii) quantify the contribution of different sites in sorption of monovalent organic cations, crystal violet (CV) and methylene blue (MB), on palygorskite and sepiolite.

The Pi sorption capacity of sepiolite and palygorskite amounted at about 0.7 and 1.5 cmol kg\(^{-1}\), respectively, which is higher than other crystalline silicate clays. Sepiolite has the potential to be a carrier for orthophosphate compounds. The IHP sorption capacity was 24 and 15 cmol kg\(^{-1}\) for sepiolite and palygorskite, respectively. The large surface area and Al-Mg contents, may explain the P sorptive behavior of these minerals.

The availability of sorbed P by palygorskite and sepiolite in the presence of calcite was compared with that of a montmorillonite, using a sequential extraction technique. About 90% of total Pi sorbed on a sepiolite-calcite mixture was recovered over seven extractions, while the recovery of sorbed Pi was about 20%, 12%, and 2% for palygorskite-calcite, montmorillonite-calcite, and pure calcite, respectively. Application or presence of sepiolite in calcareous soils may favor the phosphate availability in these soils.

The maximum sorption of MB and CV greatly exceeded the cation exchange capacity of these minerals. In sorption maxima, the neutral sites showed the highest contribution to the sorption of organic cations as compared to the free and complexed negative sites. This part of the study may help the modification of clay surfaces for different industrial applications.
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ABSTRACT

Palygorskite and sepiolite are silicate clay minerals that commonly occur with calcite in soils of arid regions. These clays have tendencies to adsorb/release phosphate (P) in the soil system. The sorptive characteristics of palygorskite and sepiolite are also used in a number of industrial applications. This study will primarily help sustainable crop production in arid and semiarid regions. It may also lead to a more efficient industrial application of these clay minerals.

The objectives of this thesis were to: i) establish the sorption isotherms and kinetics of orthophosphate (Pi) and inositol hexaphosphate (IHP) on palygorskite and sepiolite, ii) determine the chemical extractability of sorbed phosphate on palygorskite and sepiolite in the presence of calcite, and iii) quantify the contribution of different sites in sorption of monovalent organic cations, crystal violet (CV) and methylene blue (MB), on palygorskite and sepiolite.

The P sorption experiment was carried out by application of P in the range of 0.0 to 2.0 mM for Pi and from 0.0 to 10.0 mM for IHP compounds. The Pi sorption capacity of sepiolite and palygorskite amounted at about 0.7 and 1.5 cmol kg⁻¹, respectively, which is higher than other crystalline silicate clays. The IHP sorption capacity was 24 and 15 cmol kg⁻¹ for sepiolite and palygorskite, respectively. The large surface area and Al-Mg contents, may explain the P sorptive behavior of these minerals.

The sorption kinetics of Pi and IHP on palygorskite and sepiolite were modeled using a modified Freundlich equation. The data indicated the occurrence of a fast and a slow sorption process. The availability of sorbed P by palygorskite, sepiolite and a montmorillonite, in the presence of calcite was investigated, using a sequential extraction technique. About 90% of total Pi sorbed on a sepiolite-calcite mixture was recovered over seven extractions, while the recovery of sorbed Pi was about 25%, 20%, and 5% for a palygorskite-calcite, montmorillonite-calcite and pure calcite, respectively.
Sorption of organic cations, MB and CV, on palygorskite and sepiolite were also examined. The maximum sorption of MB and CV greatly exceeded the cation exchange capacity of these minerals. This shows that, besides the free negative sorption sites, the sites satisfied with sorption of single cations and neutral sorption sites on the clay surfaces contribute to the sorption of organic cations. This part of the study may help the modification of clay surfaces in different industrial applications.
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CHAPTER 1
INTRODUCTION

1.1. BACKGROUND INFORMATION

Palygorskite and sepiolite are fibrous silicate clay minerals formed in a wide spectrum of environments. A large body of information is available on the occurrences of palygorskite and sepiolite in soils of arid and semiarid regions (Abtahi, 1980; Singer, 1989; Aqrawi, 1993; Verrecchia and Le Coustumer, 1996; Khademi, 1997).

Due to the state of various types of H₂O associated with these minerals, as well as the characteristics of their adsorption sites, palygorskite and sepiolite play an appreciable role in agrochemistry of soils in which they occur (Singer, 1989). With respect to the role of palygorskite and sepiolite in soils, research on reactions of phosphorus with these minerals is needed. The results of this study may help a sustainable crop production in soils of arid and semiarid regions.

Interactions of the major forms of phosphorus with soil constituents are important in the interpretation and prediction of fertility and in environmental aspects of phosphorus in soils. Phosphorus deficiency in plants is one of the most important soil fertility problems throughout the world. Also, the environmental impact of phosphorus on eutrophication of surface water is mainly governed by the pathways of different P-compounds in soil. In a polycomponent system such as soil, several reactive groups participate in the P adsorption-desorption processes.

The interactions of phosphates with soils and soil components have been extensively studied from various aspects: reaction products, surface complexation mechanisms, sorption and desorption equilibrium isotherms, and adsorption kinetics
(Parfitt, 1978; Sample et al., 1980; Olsen and Khasawneh, 1980; Anderson et al., 1985; Goldberg and Sposito, 1985; Bar-Yosef et al., 1988). The equilibrium isotherm of phosphate adsorption and desorption is considered a useful tool for assessing soil phosphate status and clarifying the sorption and desorption capacity of soil components (Olsen and Khasawneh, 1980; Sparks, 1986).

The kinetics of sorption reactions is also a major aspect of the interactions of phosphates in the soil environment. Sorption is a dynamic processes and a knowledge of the kinetics of this reaction is fundamental. Moreover, to understand properly the fate of different P compounds that are applied in soils with time (e.g. fertilizers, pesticides, and organic pollutants), and thus, improve nutrient availability and the quality of the soil environment, one must study kinetics. For the reactions of organic and inorganic phosphates with palygorskite and sepiolite, however, there is little information in the literature concerning equilibrium isotherms, reaction kinetics, surface adsorption mechanisms, and the availability of adsorbed compounds.

Carbonates exist along with palygorskite and sepiolite in most soils of arid and semiarid regions. Electron microscope studies have shown a close association between these two groups of minerals in which larger calcite crystals are usually covered by the relatively small and minute palygorskite and/or sepiolite fibers (Singer, 1981; Ingles and Anadon, 1991; Aqrawi, 1993; Pletsch et al., 1996; Khademi, 1997). The particle-to-particle association shows that these fibrous clay minerals provide a large reactive surface area in the soil system, even in the presence of carbonates, which may significantly influence the sorption behavior of the soil in which they occur.

The magnesium silicate composition of palygorskite and sepiolite also favors the availability of phosphate over aluminum silicate clays, such as montmorillonite, which is another major clay mineral in soils of arid regions. The presence of palygorskite and sepiolite in the soil provides notable concentrations of Si and Mg (Singer, 1989) that may enhance the availability of phosphate in the soil system. Despite the promising role of
palygorskite and sepiolite clays in the agrochemistry of soils in arid regions, quantitative information on the availability of sorbed phosphates by these minerals in a natural system is still lacking. The effect of these minerals on the reversibility of P sorption reaction may be a major concern for fertilizer application efficiency and mobility of the soil P.

In addition to their significance in the soil environment, palygorskite and sepiolite are used in over one hundred different industrial applications (Galan, 1996). One of the principal applications of these clay minerals is utilization of their sorptive properties. Several studies have revealed that the sorption maxima of organic cations on silicate clay minerals exceed their cation exchange capacity. This shows that besides the contribution of cation exchange capacity (CEC), sorption takes place on neutral sites and on the neutral complexes that form through sorption of an organic cation on a negative site (Nir, 1986; Rytwo et al., 1995). The extension of organic cation sorption to the neutral sites and neutral complexes results in charge reversal of the surfaces, that in turn alters the sorption characteristics and colloid behavior of clays (Margulies et al., 1988; Aznar et al., 1992; Boyd, 1994). Due to the large surface area and low cation exchange capacity of palygorskite and sepiolite, this phenomenon is expected to be more pronounced in these minerals. Knowledge of the quantity of different complexes and charged sites provides a better understanding of the colloid behavior which, in turn, leads to a more effective use of clay in different applications.

1.2. HYPOTHESES

Previous studies have shown that palygorskitic soils have a higher P sorption capacity than those dominated with other silicate clays (Sayin et al., 1990). Due to their large external surface area where the P sorption sites occur, it seems that the P sorption capacity of these minerals exceeds that of other silicate clay minerals. The P sorption capacity is affected by different factors including surface cations and electrolyte conditions.
Due to the high dispersability of palygorskite and sepiolite in the presence of electrolytes, the P sorption sites are readily accessible; therefore, the P sorption reaction seems to take place as a fast process, rather than by slow processes such as diffusion, which are common for aggregated colloids. The kinetics of P sorption reactions may also be affected by the surface cation and the electrolyte conditions.

The chemical composition of palygorskite and sepiolite suggests that the sorbed P on the clay surfaces is easily extractable. These silicate clays possess high Mg contents. With their relatively low affinity for P retention, the Mg atoms mostly occupy the edge positions in the octahedral layer, where the P sorption takes place. In contrast, the smaller Al atoms, with a high affinity for P sorption, mostly fill in the interior positions farther from the P sorption sites.

Due to their chemical and physical characteristics, palygorskite and sepiolite seem to play a significant role in sorption and availability of P in the calcareous environments where they occur. This may be through particle-to-particle interactions of clay with calcite present in the system or by release of Mg and Si, which inhibit the formation of insoluble Ca-phosphates. By the same mechanism, but to a lower degree, other silicate clay minerals such as montmorillonite may affect the P sorption reactions in a carbonatic system.

Organic cation sorption of palygorskite and sepiolite exceeds their cation exchange capacity; therefore, adsorption beyond the CEC of the mineral takes place on neutral sorption sites as well as sites that have been satisfied with sorption of a cation. This may result in charge reversal of colloid surfaces that affect the colloid behavior. The silanol groups (SiOH) at the edge of crystals are the most probable sites to provide the neutral sorption sites for organic molecules.
1.3. OBJECTIVES

The overall objectives of this study were to investigate:

i) the effects of electrolyte concentration, surface cation, pH, and duration of reaction on sorption behavior of palygorskite and sepiolite for selected organic and inorganic P compounds common in the soil system,

ii) the significance of these minerals on sorption and availability of P applied in a carbonatic system, and

iii) the sorption characteristics of these minerals, with reference to selected cationic and neutral organic molecules.

The specific objectives of this investigation will be given in the relevant chapters. The results of this study may contribute to better phosphorus management in carbonatic soils. It may also lead to more effective industrial applications of palygorskite and sepiolite.
CHAPTER 2
LITERATURE REVIEW

2.1. Palygorskite, Sepiolite and Interactions with Phosphates.

Palygorskite and sepiolite, although considered relatively rare minerals in soils, occur in many soils and sediments in arid regions (Singer, 1989). In the last two decades these minerals have been detected in soils from all the continents. It is generally believed that these minerals in soils are inherited from calcareous sediments rich in palygorskite and sepiolite (Lee et al., 1983; Shadfan and Mashhady, 1985; Badraoui et al., 1992). However, several workers have discussed the possibility of palygorskite formation in the soil environment (Eswaran and Barzanji, 1974; Singer and Norrish, 1974; Elprince et al., 1979; Singer, 1989; Monger and Daugherty, 1991; Botha and Hughes, 1992). While there is an abundant literature about the occurrence and possible origin of palygorskite and sepiolite in the soils of arid regions, there are few comprehensive studies that have examined the role of these clay minerals in soil fertility. In this regard the available information on interactions of these minerals with P compounds is rather limited.

2.1.1. Palygorskite and sepiolite in soils

The clay fractions of many soils and sediments younger than Lower Cretaceous in the Middle East are dominated by palygorskite, while sepiolite is rather rare in the soil and occurrences are mainly in parent materials. The occurrence of palygorskite in soils has been reported from Saudi Arabia (Elprince et al., 1979; Lee et al., 1983; Mackenzie et al.,
1984; Shadfan and Mashhady, 1985), Iraq (Aqrawi, 1993), Israel (Yaalon and Wieder, 1976; Singer, 1981; Verrecchia and Le Coustumer, 1996), Jordan (Shadfan and Dixon, 1984; Shadfan et al., 1985), Syria (Muir, 1951), and Egypt (Elgabaly, 1962; Hassoubba and Shaw, 1980). In a study from central Iran, Khademi (1997) reported that palygorskite is the most dominant clay mineral followed by mica, chlorite and kaolinite in the calcic and gypsic horizons. Surface soil, however, contains more mica, chlorite, and kaolinite and less palygorskite. In the same study, sepiolite was reported as a dominant clay mineral in the parent materials.

Palygorskite-containing soils are usually calcareous throughout and mildly alkaline. Calcite is the most common carbonate, although some Saudi Arabian Torrifuvents also contain dolomite (Mashhady et al., 1980). Soil pH values typically vary between 7.5 and 8.0. A Natrixeralf containing palygorskite was reported in southern Iran with a pH exceeding 8.0 (Abtahi, 1977), but according to Eswaran and Barzanji (1974) maximum development of palygorskite in a group of soils from Iraq was at pH 7.9. Palygorskite-bearing soils of this type are also highly saline.

The conditions necessary for palygorskite neoformation have been specified as high Si and Mg activity, with a pH of about 8.0 (Velde, 1985; Singer, 1989), while sepiolite forms when Al concentration is low and appreciable amounts of Mg are available. As a result of calcite precipitation in the soil, the Mg/Ca ratio of the soil solution would increase. Such a process has been described by Botha and Hughes (1992) and Rodas et al. (1994). Also in the calcrete medium, the alkaline conditions facilitate silica mobility, which can promote the formation of palygorskite mainly at the contact point with silica grains. At these sites the solutions circulate preferentially and thin water films remain for the longest period during the evaporation phase. The silica necessary for the neoformation of palygorskite is likely derived from the weathering of existing silicates.

Although the environment under which pedogenic carbonate is formed provides a buffered alkaline condition that is needed for palygorskite formation, the close proximity
of calcite is probably unnecessary (Yaalon and Wieder, 1976). A possible connection between secondary calcite and palygorskite is the action of the former in maintaining a high Mg level through the precipitation of calcite (St. Arnaud and Herbillon, 1973). The petrocalcic horizon studied by Monger and Daugherty (1991) was dominated by palygorskite. These workers suggest that petrocalcic horizons, may foster palygorskite neoformation, because they are the site of high Mg content and abundant sand and silt grain dissolution. Palygorskite was found in all the Kalahari calcrite profiles analyzed by Watts (1980); in some cases, the mineral constituted over 90% of the less than 2μm acid insoluble fraction and up to 6% of the bulk samples.

2.1.1.1. Structural characteristics of palygorskite and sepiolite

The specific behavior of palygorskite and sepiolite in sorption/desorption reactions arises from their structural characteristics. The structures of both palygorskite and sepiolite contain continuous planes of tetrahedral basal oxygen atoms approximately 0.65 nm apart. The apical oxygens point alternatively up and down relative to the planes of basal oxygens in a pattern such that the tetrahedra pointing in the same direction form ribbons that extend in the direction of the a-axis (Figure 2.1). The ribbons have an average width along the b-axis of three linked tetrahedral chains in sepiolite and two linked chains in palygorskite. Ribbons with apices pointing up are linked vertically to ribbons with apices pointing down by forming octahedral coordination groups around Mg and Al. Two-to-one layers that are continuous along the a axis, but of limited lateral extent along b axis, are thus formed (Bailey, 1980).

Isomorphous substitution of Al for Si in the tetrahedra is very limited in both minerals. Aluminum and Fe replace Mg in the octahedral sites. Iron and, to a lesser extent, Mg tend to occupy edge positions in palygorskite (Heller-Kallai and Rozenson, 1981; Singer, 1977), whereas the interior positions are occupied predominantly by the smaller Al ion. Ferric ions in edge positions have a regular six-coordination.
Figure 2.1. Projection of (A) palygorskite structure, and (B) sepiolite structure
(from Singer, 1989)
A small number of exchangeable Ca$^{2+}$ and Mg$^{2+}$ cations and variable amounts of zeolitic H$_2$O are contained in the rectangular channels that lie between the backs of opposing 2:1 ribbons and extend parallel to the fiber direction (Figures 2.1 and 2.2).

In addition to zeolitic H$_2$O, four bound-water molecules (OH$_2$) per formula unit are located at the edges of the ribbons (Figure 2.1), held more tightly because they participate in the coordination of the octahedral Mg and Al (Bailey, 1980).

The total surface area of palygorskite and sepiolite computed from structural models is about 8 to 9 x 10$^5$ m$^2$ kg$^{-1}$, including the surfaces of the channels (Serna and Van Scoyoc, 1979). Due to the presence of wedge-shaped capillaries and channels, the available surface area depends strongly on the nature (size, shape, and polarity) of the molecules used as sorbate. It is calculated that as much as 60% to 70% of the surface area in both palygorskite and sepiolite corresponds to micropores.

![Figure 2.2. Three dimensional projection of (A) mica type mineral, (B) sepiolite, (C) and (D) palygorskite (from Singer, 1989).]
2.1.1.2. Active sorption centers on palygorskite and sepiolite

There exist at least three types of sorption sites on palygorskite and sepiolite surfaces (Figure 2.3):

1. Oxygens on the tetrahedral sheets of the ribbons behave as weak electron donors and display a weak interaction with sorbed species.

![Diagram of palygorskite model](image)

Figure 2.3. Palygorskite model. (a) The dioctahedral character. (b) Coordinated $H_2O$. (c) Si-OH groups (from Singer, 1989).
2. Water molecules are coordinated to Mg ions at the edges of structural ribbons at a ratio of 2 H$_2$O for each Mg$^{2+}$; one of the protons on each molecule can form a H-bond directed towards the hexagonal holes of oxygens that are created by the Si-O-Si connections between the amphibole chains.

3. SiOH groups are associated in large numbers with terminal Si tetrahedra at the external surfaces; broken Si-O-Si bonds compensate their residual charge by accepting H$^+$ or OH$^-$ and become Si-OH groups. The abundance of these groups is related to the dimensions of the fibers and crystal imperfections. These groups are less abundant in palygorskite than in sepiolite. The Si-OH groups may interact with molecules adsorbed on external surfaces, particularly with organic reagents.

2.1.2. Phosphorus in soils

Total phosphorus (P) content of soils ranges from approximately 0.2 to 5 g kg$^{-1}$, with an average of 0.5 g kg$^{-1}$. Phosphorus in soil is present as organic and inorganic phosphorus. Soil P can be divided into four general categories: (1) P in soil solution; (2) P adsorbed on the surface of inorganic soil constituents; (3) P in minerals, both crystalline and poorly crystalline; and (4) P as a component of soil organic matter. A large fraction of P in surface soils is organic and adsorbed P (Lindsay et al., 1989). There exist dynamic relationships between the different forms of P and adsorbed P. All forms of P can be subject to adsorption and/or desorption by soil mineral particles.

2.1.2.1. Interactions of organic phosphates with soil minerals

Studies show that clay minerals, soil clays, and metal oxides are very active in adsorbing organic phosphates commonly found in soils (Anderson et al., 1974; McKercher et al., 1986). Organic P may exist in different forms. However, of the organic P compounds identified in soil, inositol phosphates form the major part. Nucleic acids and phospholipids are also present in smaller quantities.
Inositol phosphates can be strongly sorbed by clay minerals and sesquioxides (Anderson et al., 1974; McKercher et al., 1986). The degree of sorption by a specific sorbent increases with the number of phosphate groups (Anderson and Arlidge, 1962). Compared to orthophosphate, inositol hexaphosphate was found to be preferentially adsorbed by some acidic Scottish soils (Anderson et al., 1974). Nucleic acids, phospholipids and simple sugar phosphates are also adsorbed by various soil components, but to much lower extent (Greaves and Wilson, 1969; McKercher et al., 1986).

The phosphate in inositol hexaphosphate can be readily utilized by plants grown in water or sand cultures, but in soil or soil-sand media the availability is low. In acid soils this has been attributed to adsorption by clay minerals, and the formation of insoluble salts. Goring and Bartholomew (1950) studied the sorption of inositol hexaphosphate by bentonite, kaolinite, and illite over the pH range 3.0 to 7.5, and found maximum sorption between pH 3.5 and 4.5.

2.1.2.2. Interactions of inorganic phosphates with soil minerals

Inorganic (ortho-) phosphate is also subject to strong adsorption on the surface of oxides/hydroxides of Al and Fe, and on the edges of clay minerals. Sorbed phosphate may be present on surfaces of soil particles and as separate precipitates. The retention of phosphate by specific soil constituents has been reported by many researchers (Parfitt, 1978; Sayin et al., 1990). Sree Ramulu et al. (1967) studied the adsorption of phosphate by 12 acid soils containing various amount of Fe oxides and obtained significant correlation between P retention and the contents of dithionite or oxalate extractable Fe. In highly weathered soils, kaolinite or crystalline oxides of Al and Fe are usually responsible for phosphate adsorption (Jones, 1981; Karim and Adams, 1984).

In a study on the soils of Ugurlu series (Paleustollic Torrent) from an area in southeastern Turkey, Dinc (1988) showed that sorption maxima correlated with the
dominant clay mineral. Palygorskite-rich soils were found to have a higher sorption capacity than smectite-rich soils. In the soil studied, palygorskite was concentrated in the clay-sized fraction, especially in the fine clay. High sorption capacity of the fine clay was, in part, related to this constituent.

2.1.2.3. Factors affecting phosphorus adsorption in soil

Phosphate adsorption by soil colloids is influenced by several factors. Ionic strength (Ie), activity of hydrogen ion (pH), presence of organic ligands, P concentration, equilibration time, and the type of adsorbed cation were studied by many researchers as factors controlling P adsorption (Traina et al., 1986; Kafkafi et al., 1988; Hue, 1991; Ioannou et al., 1994). Using KCl electrolyte, Bar-Yosef et al. (1988) showed that increasing the Ie increased P retention by the surface of kaolinite and montmorillonite. Increased Ie restricts the extent of the diffuse double layer (DDL) and consequently reduces the masking of P adsorption sites on clay edges that is induced by the negative electric field of clay faces.

Soil (pH) is an important factor controlling maximum levels of phosphate adsorption. It is often found that sorption of phosphate decreases if the pH is increased (reviewed by Sanchez and Uehara, 1980), but the effects only become large if high pH values are used. In a study of phosphate adsorption by kaolinite, Muljadi et al. (1966) suggested that if the pH of the kaolinite suspension is increased, due to dissociation of the coordinated water molecules, the negative charges of the clay edge will increase. This, in turn, increases the mutual repulsion between phosphate ions in the solution and hydroxyl radicals of the clay edges and decreases the phosphate adsorption. Conversely, hydroxyl groups are protonated at lower pH values, which is likely to increase the phosphate adsorption.
The effect of pH on P adsorption is attributed mainly to three mechanisms (Muljadi et al., 1966; Murrman and Peech, 1969; Bowden et al., 1980; and Traina et al., 1986):

(i) its effect on the relative fraction of the various P species, which differ in their affinity to the adsorbent,

(ii) the variations in charge density of clay edges with pH, and

(iii) the competition between OH⁻ and P on common adsorption sites.

The effect of pH on edge-to-face flocculation, which may affect P accessibility to clay mineral adsorption sites, however, is rarely emphasized in the literature. Traina et al. (1986) obtained an increase in P solubility in montmorillonitic soil separates when decreasing the pH from 6.5 to 4. They attributed the enhanced P concentration in the solution to the pH effect on the solubility of the solid phase, Al(OH)₂H₂PO₄.

Organic ligands may either increase or decrease the P adsorption. Kafkafi et al. (1988) showed that oxalic acid masked some sites (9-19%) available for phosphate adsorption. This resulted in the release of more P in the solution as compared to that found in the presence of Cl⁻. In contrast to oxalic acids, acetate and amino acids can increase the P adsorption to the clays. These compounds cause a decrease in interlamellar spacing through H-bonding of amino groups which, in turn, reduce the negative surface charge for clay particles and allow easier approach of the phosphate ion to the edge reaction sites of clay.

2.1.2.4. Mechanisms of phosphate sorption

To explain phosphate adsorption by mineral particles, different mechanisms are suggested. Kafkafi et al. (1967) suggested that the bond between the phosphate and the surface of a mineral is at least partly covalent in that there is a sharing of a proton with the surface, leaving a small additional negative charge on the H₂PO₄⁻ grouping. It is suggested that this link of the phosphate with the surface is a surface neutralization
reaction. Considering the electronegativity values of Al, H, and O, which are 1.5, 2.1, and 3.5, respectively, Kuo and Lotse (1974) suggested that a covalent bond is formed between Al of the surface and O of the phosphate ion rather than between Al and H. In order to explain the increase of negative charge as a result of phosphate adsorption, they proposed that phosphate ions replace coordinated H₂O groups and/or coordinated anions to form an outer octahedral complex of aluminum phosphate. When kaolinite is in contact with a phosphate ion, Al may use one vacant d orbital to hold one pair of electrons donated by oxygen of the phosphate ion. The adsorption is illustrated in Figure 2.4.

Figure 2.4. Phosphate adsorption by kaolinite (from Kuo and Lotse, 1974)

Among the mechanisms by which sorption processes occur, the three principal ones are: (1) adsorption, an accumulation of matter at the interface between a solution and a solid absorbent without the development of matter at a three-dimensional molecular arrangement; (2) precipitation, the growth of a solid phase exhibiting a primitive molecular unit (a complex) that repeats itself in three dimensions; and (3) absorption, the diffusion of a chemical species into a solid phase (Sposito, 1986).

Most researchers reported that at high concentration of phosphate, the retention of phosphate by soil colloids could be through precipitation. Russel and Low (1954) concluded that adsorbed aluminum precipitates the phosphate as an aluminum phosphate
on the kaolinite surface. Olsen and Watanabe (1975) suggested that phosphate ions become attached to exchangeable iron, aluminum and calcium ions, or to those same ions held in the outer edges of the lattice. Kittrick and Jackson (1956) stated that kaolinite reacts with phosphate by chemical precipitation to form separate-phase phosphate crystals. Hsu (1965) also suggested that adsorption is a special case of precipitation in which aluminum (or iron) remains as the constituent of the original phase but reacts with phosphate by use of residual force on the surface.

The specific adsorption of phosphate (or formation of inner-spherical complex) by soil mineral components is characterized by the fact that the adsorption is not determined by the properties of the diffuse double layer or charge character of surfaces. The consequences of specific adsorption of phosphate are: increase in the negative charge on surfaces, release of ligands (especially OH) coordinated to surface sites, and irreversibility of adsorbed phosphate. Specific adsorption of phosphate has been indirectly indicated by a comparison of adsorption of a non-specifically adsorbed anion, such as chloride with phosphates. The adsorption of chloride becomes zero at pH values for which the surface takes the negative charge (Mott, 1981). Phosphate adsorption, however, continues regardless of the sign of the surface charge or suspension pH, showing a steady increase in adsorption with equilibrium concentration of phosphate (Breeuwsma and Lyklema, 1973).

2.1.2.5. Phosphate sorption sites

Several studies suggested that the same active sites in soils were involved in sorbing organic phosphates and orthophosphate (McKercher and Anderson, 1968; Anderson et al., 1974; Evans, 1985). The reaction sites for anion adsorption in pure systems (e.g., a silicate clay mineral or oxides of Al and Fe) are the singly coordinated Al-OH and Fe-OH groups which are exposed at surfaces (Parfitt, 1978). These groups are present at the edges of clay minerals, as well as on the surfaces of hydrous oxides,
and are, therefore, present in soils (Greenland and Mott, 1978). The sites adsorb protons at low pH creating positive charges and deprotonate at high pH creating negative charges, as depicted by Rajan et al. (1974):

![Chemical Reaction Diagram]

where M represents the metal ions Al(III) and Fe(III). Lewis acid sites Al-OH$_2$ and Fe-OH$_2$ also occur on the edges of minerals. At high pH these sites become negatively charged (Parfitt, 1978):

$$\begin{align*}
\text{M-OH}_2 & \rightarrow \text{M-OH} \quad + \text{H}_2\text{O} \\
\end{align*}$$

The hydroxyls coordinated to two metallic ions, M-OH-M, are usually not acid in specific adsorption although they can form H-bonds (Parfitt, 1978). Rajan (1976) proposed a breakage of the hydroxyl coordinated to two Al(III) ions to explain the phosphate adsorption beyond the adsorption maximum:

$$\begin{align*}
\text{Al} & \quad \text{OH} \quad \text{H}_2\text{O} \quad -0.5 \\
\text{Al} & \quad \text{OH} \quad \text{Al-OH} \quad + \text{Al-OH}_2 \quad +0.5
\end{align*}$$

The above discussions clearly show that the pH of adsorption systems can dictate the nature of phosphate sorption sites to a great extent.

### 2.1.2.6. Appraisal of phosphate adsorption processes

Phosphate sorption reactions with soil components can be assessed by using different approaches e.g., equilibrium sorption isotherms, kinetic studies and chemical fractionation (Sadler and Stewart, 1977; Sparks, 1986).
The relationship between the amount of P adsorbed per unit weight of soil (X) and the equilibrium P concentration in solution (C) bathing the soil at a constant temperature has been described by several adsorption isotherms. The main motivations for describing adsorption curves are to: i) identify the soil constituents involved in adsorption, ii) predict the fertilizer needed to meet the demand of plant uptake for an optimum yield, iii) study the nature of the adsorption process to learn more about the mechanism of the process (Sanyal and Datta, 1991).

Several adsorption equations have been developed to describe the removal of phosphorus from dilute solutions by soils or soil constituents. The classic Freundlich, and Langmuir equations have been used most frequently. To include different factors that specifically affect the P sorption, modified forms of these equations have also been introduced (Muljadi et al., 1966; Goldberg and Sposito, 1984; Kuo, 1988).

The Freundlich adsorption equation is an empirical relationship between the amount adsorbed of substance per unit mass of adsorbent, X/M, and the aqueous concentration, [C], in the form:

$$\frac{X}{M} = K [C]^{1/n}$$

where K and n are positive constants, n being greater than unity in most cases of practical interest. The Freundlich equation can also be written in the following form:

$$\log (\frac{X}{M}) = \log K + \frac{1}{n} \log [C]$$

It can be seen that when experimental data follow a Freundlich isotherm, a plot of Log (X/M) against Log [C] should yield a straight line with a slope equal to 1/n and an intercept equal to LogK. Such a Log-Log plot is referred to as a "Freundlich plot".

The Langmuir equation as used in soil science may be represented as follows:
\[ \frac{X/M}{1 + K [C]} = K A \]  

where the Langmuir constant, \( K \), is a measure for the binding strength of the adsorption sites for molecular species and \( A \) is defined as the adsorption maxima. The Langmuir equation can also be written in the linear form:

\[ \frac{[C]}{X/M} = \frac{[C]}{A} + \frac{1}{K A} \]

from which it can be seen that a plot of \( [C]/(X/M) \) against \( [C] \) ("Langmuir plot") yields a straight line with an intercept of \( 1/KA \) and a slope of \( 1/A \). Although there seems to be no general theoretical justification for the use of the Langmuir equation to describe adsorption of molecular species in soils, it is easily shown that any type of adsorption approaching saturation with increasing aqueous concentrations can be approximated with a Langmuir isotherm. This is the simplest mathematical expression satisfying the following requirements:

\[ X/M = 0 \quad \text{at} \quad [C] = 0 \]

\[ \lim_{[C] \to \infty} X/M = A \]

A specific form of the Langmuir equation applied by Muljadi et al. (1966) for describing P adsorption of gibbsite is as follows:

\[ X/M = A_1 + \frac{K A_2[C]}{1 + K [C]} \]

The equation describes almost the same conditions as those of the Langmuir equation. Here, \( A_1 \) is the adsorption maxima at the higher affinity region and \( A_2 \) describes the adsorption at the lower affinity region.
The kinetic investigation of phosphate adsorption and desorption is considered as a useful tool for assessing soil phosphate status and clarifying reaction mechanisms (Sparks, 1986). Adsorption and desorption of phosphate in a soil system are time dependent processes. The general pattern of phosphate adsorption-desorption shows that the reaction is rapid initially, operating on time scale of minutes or hours, then diminishes in rate gradually, on time scales of days or weeks (Kuo and Lotse, 1972; Rajan and Fox, 1972; Hingston, 1981). Thus, the phosphate adsorption and desorption processes are often arbitrarily divided into fast reaction and slow reaction. A general pattern of P adsorption by CaCO$_3$ and Ca-kaolinite as a function of time is illustrated in Figure 2.5.

![Graph showing phosphate concentration and reaction time for CaCO$_3$ and Ca-kaolinite](image-url)

**Figure 2.5.** Phosphate adsorption by (a) CaCO$_3$ and (b) Ca-kaolinite as a function of time (from Kuo and Lotse, 1972).
Adsorption is rapid at the beginning. When about 80% of the adsorption maximum for each concentration is reached, the curve levels off.

For a complete adsorption-desorption reaction, the following reaction steps can be envisaged:

1. Diffusion of phosphate ions through the solution film which surrounds the adsorbent particles;
2. Diffusion of phosphate ions through or into surface pores or aggregates;
3. Adsorption or desorption of phosphate ions on particle surfaces;
4. Diffusion of desorbed phosphate ions away from the surface through intra-particle space;
5. Diffusion of desorbed phosphate ions into the bulk solution through solution films.

The kinetics of phosphate adsorption/desorption are governed by the slowest reaction step, termed the rate-limiting step, which could be one of the above reactions or the coupling effect of two or more reactions. Thus, it was suggested that for an adsorption reaction, the adsorption rate \( r_a \) can be expressed as:

\[
r_a = k_1 + k_2 + k_3
\]

where \( k_1 \) is rate constant associated with film diffusion process; \( k_2 \) intra-particle diffusion and \( k_3 \) a chemical reaction (Sparks, 1986). For reactions occurring in liquid systems at constant volume, reaction rate is expressed as the number of reactant species (molecules or ions) changed into product species per unit of time and per unit of volume of the reaction system. Rates are expressed as a decrease in reactant concentration and/or increase in product concentration per unit time. Information on kinetics of phosphate adsorption by palygorskite and sepiolite is rare.

Modeling reactions kinetically is a useful approach for predicting the fate of applied fertilizers, pesticides, and toxic organics with time in soil and aquatic environments (Sparks, 1986). The study of the kinetics of phosphate adsorption and
release by minerals has been concentrated on two aspects: to find suitable expression to describe the kinetics and to clarify aspects of the mechanisms of the process. To describe the kinetic process of phosphate sorption, two empirical equations frequently used for fitting experimental data are the modified Freundlich equation (Kuo and Lotse, 1974) and the Elovich equation (Chien and Clayton, 1980; Sharpley, 1983). Chemical kinetic equations such as the first and second order kinetics and the parabolic diffusion equation have also been fitted to phosphate sorption data (Evans and Jurinak, 1976). The parameters of these equations have been used to interpret the mechanism of the reaction of phosphate with soils.

First order kinetics assumes that the rate of change in concentration is proportional either to the phosphate concentration in solution or to the number of empty sites (Ainsworth and Summer, 1985; Elkhatib and Hern, 1988). The assumption of second order kinetics is that the rate of change in concentration is proportional to both the phosphate concentration in solution and the number of empty sites, or is only proportional to the 2nd power of the concentration in solution (Kuo and Lotse, 1972; Griffin and Jurinak, 1974). The rate of phosphate adsorption by CaCO₃ and Ca-kaolinite is described by a second-order kinetic equation that considers the simultaneous change in phosphate concentration and the change in surface unsaturation sorbed by displacing coordinated water molecules and/or coordinated anions.

Olsen and Watanabe (1975) pointed out that the theoretical basis for the application of the Langmuir equation to the adsorption of ions by solids is not fully developed. In developing a kinetic equation for phosphate adsorption it was first concluded from the Langmuir plot of the experimental data that the energy of adsorption does not vary with the surface coverage. Thus, the fact that the experimental points fit a straight line indicates that the energy of adsorption, which can be obtained from the Arrhenius equation, is constant under isothermal conditions. A curvature indicates that the
bonding energy is not constant and that there is no well-defined maximum (Bache and Williams, 1971).

### 2.1.2.7. Availability of adsorbed phosphate

Information on the bioavailability of surface phosphate complexes is essential to understand fully the nature of these complexes. Bioavailability of inorganic and organic phosphates is related to the type of associated cations. Sodium and calcium salts of inorganic and organic phosphates are readily available as the P source to microorganisms, whereas iron and aluminum salts have much lower availability (Greenwood and Lewis, 1977). Parfitt (1979) showed that orthophosphate adsorbed on goethite was available to rye plants. The availability of organic phosphates likely depends on the nature of phosphate bonding, the level of P addition, the sorption capacity, and pH of the soil. In acid soils, the availability of adsorbed inositol hexaphosphate was apparently dependent on the contents of amorphous Al and Fe (Anderson et al., 1974).

Phosphates dissolved in soil solution are the immediate nutrient source for plants, however, only a small part of the P taken up by a crop is present in soil solution at any time. Therefore, plant P supply depends largely on the utilization of P bound to the solid soil phase. The sorbed P (Jungk et al., 1993) may become available in the soil solution through different mechanisms. Organic acids and ligands present in soil solution induce the desorption of sorbed phosphate. The depletion of the solution phosphate is another important mechanism regulating the diffusion of phosphate from the sorbed phase into the soil solution.

Although organic acids may be short-lived in soils, their continual production from decomposing organic matter, root exudate, and microbial metabolites makes these acids and their conjugated anions chemically important. These molecules interact with soil minerals and modify the soil characteristics (Moshi et al., 1974; Earl et al., 1979; Hue, 1991). The total concentration of complexing organic acids in soil solution is estimated to
be $10^{-5}$ to $10^{-4}$ M; however, in the localized zones where biological activities are intense, such as in the soil rhizosphere and near decomposing plant residues, the organic acids produced may reach a concentration of $10^{-3}$ M or higher (Mullette et al., 1974; Lopez-Hernandez et al., 1979).

It has been reported extensively that the presence of different organic ligands such as citrate, malate, and oxalate significantly increases the desorption of P from different minerals. Desorption of P may have been enhanced by the carboxyl and hydroxyl functional group through ligand exchange (Dinkelaker et al., 1989). The competitive adsorption of organic anions with phosphate for adsorbing sites can explain this effect (Appelt et al., 1975; Lopez-Hernandez et al., 1986). The released ligands from plant roots may also enhance the desorption of P by dissolution of P sorbing surfaces (Lopez-Hernandez et al., 1986; Jungk et al., 1993; He et al., 1994). Complex formation between organic acids/anions and Fe or Al components of the soil is believed to cause this effect (Appelt et al., 1975). Thus, those molecules containing several functional groups (e.g., OH, COOH), which are capable of forming stable complexes with metals, would reduce P retention more effectively than those containing few groups (Appelt et al., 1975; Lopez-Hernandez et al., 1986).

Soil solution P is replenished by release from the solid phase, particularly by desorption. In this way plants induce the mobilization of sorbed P. In a given soil, the final depletion of solid phase P depends on the P exhaustion of the liquid phase caused by the plant. Jungk et al. (1993) reported that in a flowing solution culture, plants exhausted the P concentration to less than 0.1 μmol L$^{-1}$. In a typical depletion profile of soil solution P in the rhizosphere of a 3-day old maize root segment in a sandy soil, solution P concentration, at the interface, dropped to about 4% of its value in the bulk solution. This means that plant roots create almost the maximum possible gradient, which is the driving force for both desorption and diffusion (Jungk et al., 1993). Taylor and Kunishi (1971) and McCallister and Logan (1978) also reported that the sediment-bound P becomes
available by desorption when algae reduce the soluble P concentration in the water below that of the equilibrium P concentration of the sediment P.

In this thesis, the desorbability of sorbed P was assessed by sequential extraction of the P loaded samples with fresh solution.

2.1.2.8. Phosphorus desorption Q/I curves and related parameters.

Desorbability of sorbed P on soils may be assessed using desorption isotherms or Q/I curves (Brewster et al., 1975; Barrow, 1979; and Raven and Hossner, 1993). A hypothetical P desorption Q/I curve and the parameters derived from it are shown in Figure 2.6. In this figure the cumulative desorbed P (Q), by a sequential extraction, is presented against the equilibrium P concentration in the solution (I). Different parameters may be derived from this curve e.g., Qmax, Io, and BPo. The Qmax or maximum desorbed P, a quantity parameter, is the amount of cumulative P extracted from the sample after the final extraction. The Io is defined as the solution P concentration of a given sample when no P had been depleted from the solution, and is the solution P concentration equilibrated with the first P extracting solution. The buffering power refers to the slope of the Q/I curve. Because of the curved nature of the Q/I plot, the value of the buffering power depends on I or Q. The BPo is the slope of the Q/I curve at Io and is a characteristic feature of each sample. Because BPo values are negative and only the magnitude is important, the absolute value of BPo (|BPol|) may be used as a P buffering parameter. The |BPol| is defined as the amount of P desorbed per unit decrease in the solution P concentration at Io.
2.2. Interactions of clay minerals with organic molecules

The study of interactions between clay minerals and organic substances in soil science was initiated in the decade 1930-1940. Experiments involving simple organic chemicals and pure bentonite clay showed that the exchangeable inorganic cations could be replaced by organic cations, and that uncharged polar compounds could enter the interlayer space without cations being released (Gieseking 1939; Greene-Kelly 1955). The sorption maxima of organic cations exceed the cation exchange capacity (CEC) of clay minerals, showing that besides the contribution of CEC, sorption takes place on neutral sites and the neutral complexes that are formed through sorption of an organic cation on a negative site (Nir, 1986; Rytwo et al., 1995). This phenomenon would result in charge reversal of clay surfaces which, in turn, alters the colloid behavior (Margulies et al. 1988).
2.2.1. Significance of organo-clay complexation

Interactions of clay minerals with organic molecules are of concern from different aspects. The interactions between silicates and organic cations are ecologically important, because they are responsible for the fate of many agrochemicals in soils and ground water (Zielke et al., 1989). The adsorption of organic cations on clays changes the nature of the clay surface, transforming it from hydrophilic to hydrophobic (Boyd, 1994). The modified clay surface can adsorb organic molecules of low solubility in water (Zhang et al., 1993). The increased threat of environmental pollution by pesticides and other organic pollutants has promoted investigations on the use of organo-clays as sorbents for organic molecules (Jaynes and Boyd, 1991; Cornejo and Hermosin, 1995).

In most industrial applications the clay surfaces are modified by means of organo-clay complexation. The surface-modified clay usually contains surface active agents such as cationic or non-ionic surfactants that are essential for specific physico-chemical behavior. For example, organo-cation-modified palygorskite and sepiolite have been used to stabilize pesticides and to reduce their volatilization and photo-decomposition (Margulies et al., 1993; 1994). Polubesova et al. (1997) also reported that benzyltrimethylammonium (BTMA) and benzyltriethylammonium (BTEA) are quaternary amine monovalent cations that can be effective in altering the surface of the clay for the enhanced adsorption of non-polar organic molecules from water. Neutral surfactants, however, may be applied to modify the rheological behavior of clay minerals. Aznar et al. (1992) reported that modification of clay surfaces by adsorption of neutral surfactants provides stable gels of sepiolite in water and saline solutions, as well as in organic solvents.

The efficient use of clay minerals in different applications needs elucidation of the adsorption mechanisms and prediction of the surface changes due to complexation of organic molecules and the clay mineral. The nature of the various types of clay-organic interactions has been widely reviewed (Lagaly, 1984; Yariv, 1988; Boyd, 1994). Many
studies have been reported on the adsorption of cationic organic dyes to negatively charged smectites (Cenes and Shoonheydt, 1988; Dobrogowska et al., 1991).

2.2.2. Modeling of organo-clay complexation

The mechanisms of adsorption of monovalent organic cations, methylene blue (MB) and crystal violet (CV) dyes, and divalent cations (diquat and paraquat) on montmorillonite have been studied by Rytwo et al. (1995,1996). They employed an adsorption model combining specific binding and the electrostatic Gouy-Chapman equations in a closed system (Nir et al., 1994). Their model combined three main considerations:

i) consideration of specific binding; it assumed that the total amount of cation adsorbed consists of

(a) cations tightly bound to the surface, and
(b) cations residing in the double layer region;

(ii) the electrostatic Gouy-Chapman equations are solved for a suspension containing several cations of various valencies, and particles whose surfaces are charged and partially neutralized by cation binding, and

(iii) the concentration of surface sites is explicitly taken into account since it affects the depletion of cations from solution as a result of adsorption.

The main purpose of this approach was to establish a procedure that can predict the solution and adsorbed concentrations of cations. This procedure also provided predictions for surface potentials and for the amounts of cations tightly bound, as well as those of cations concentrated in the double layer region.

The adsorption of organic cations to negatively charged clay minerals was described by two binding coefficients. The first, $K_i$, describes the formation of a neutral complex between one organic cation and one clay mineral site, whereas the second, $\bar{K}_i$, refers to the binding of an organic cation and the neutral complex. The values of the binding
coefficient Ki for MB were at least $10^8$ M$^{-1}$, i.e., about six orders of magnitude higher than those of inorganic cations such as Na$^+$ (1 M$^{-1}$), Cs$^+$ (200 M$^{-1}$; Nir et al., 1986), and Cd$^{2+}$ (10 M$^{-1}$; Hirsch et al., 1989). When the amounts of dye were less than those required to saturate the exchange sites of montmorillonite, complete adsorption of MB was observed, even at very large ionic strengths (0.5 M). At higher concentrations, dye adsorption exceeded the CEC and charge reversal was observed (Margulies et al., 1988).

2.2.3. Sorption of organic molecules for surface characterization

Different organic cations are widely applied for surface characterization of silicate clay minerals. Mermut (1994) reviewed the efficiency of alkylammonium cations in surface charge measurements. The sorption of dye compounds, e.g., methylene blue (MB) and crystal violet (CV), also provides accurate information on clay surface characteristics. The sorption of MB on clays gives data on the cation exchange capacity, the surface area of clay minerals, the presence of acid sites at the clay surface, and on the external and internal surface of clays (Bodenheimer and Heller, 1968; Hang and Brindley, 1970; Rytwo et al., 1991; Wang et al., 1996).

In addition to organic cations, sorption of neutral molecules such as crown ethers may be of interest because of their contribution in formulation of pesticides (Matolcsy et al., 1981; Gunter and Johnston, 1990). Triton-X100 also is a neutral organic molecule that is widely used as a surfactant (Gerstl and Yaron, 1981). Sorption of neutral molecules may also provide useful information on the quantity of neutral sorption sites that may contribute in sorption of charged organic molecules.

2.2.4. Neutral sorption sites on palygorskite and sepiolite

Many studies concluded that neutral silanol groups (Si-OH) of palygorskite and sepiolite can react directly with organic reagents to form compounds with true covalent
bonds between the mineral substrate and the organic reactant (Ruiz-Hitzky and Fripiat, 1976; Casal Piga and Ruiz-Hitzky, 1977; and Hermosin and Cornejo, 1986). Using infra-red (IR) spectroscopy, Ahlrichs et al. (1975) illustrated the presence of Si-OH groups at sepiolite crystal edges. Similar Si-OH groups were found in palygorskite. In this study the lower intensity of the Si-OH band in palygorskite was attributed to less edge surface or fewer imperfections than was observed for the sepiolites. The difference suggests a higher sorption capacity for sepiolite with respect to sorption of neutral organic molecules.
CHAPTER 3
CHARACTERIZATION AND PURIFICATION OF PALLYGORSKITE AND SEPIOLITE

3.1. INTRODUCTION

The general structure and mineralogical properties of palygorskite and sepiolite are well known (Van Olphen and Fripiat, 1979; Singer, 1984; 1989). However, detailed mineral characteristics may vary in different samples. In this chapter some physical, chemical, and mineralogical characteristics of samples that were used in the thesis work are presented.

Relatively pure, mineral separates are needed to study the behavior and interaction of their functional groups. Samples from geological deposits are usually good candidates for this purpose, however, due to the presence of impurities, purification treatments must be carried out initially in almost all cases. The procedure suggested by Jackson (1979) is still widely used to isolate silicates from carbonates, organic materials, and iron oxides. Further purification using specific procedures may be required, however, one should consider that treatments, especially chemical ones, can alter the nature of the mineral concerned.

3.2. MATERIALS AND METHODS

The samples of palygorskite from Florida (CMS source clay minerals PFI-1) and sepiolite from Eskishehir, Turkey were characterized and purified for the sorption/desorption studies as described below.
3.2.1. Physical and chemical characteristics

Surface area of the two minerals, was measured using the BET method and nitrogen gas as adsorbate (Brunauer et al., 1938). An Autosorb-1 Quantachrome instrument was used for the measurements. Since the phosphate sorption/desorption reactions mostly occur at the crystal edges, the external surface area that is measured by the BET method seems to provide a realistic indication of the mineral P sorption capacity. The changes in surface area after sorption reactions may also explain the sorbate-mineral interactions.

To determine the elemental composition of the minerals, two replicates of 0.5 g clay were digested in a MDS-200 microwave oven (Sawhney and Stilwell, 1994). The digested samples were then analyzed using an Elan Elmer 5000 inductively coupled plasma mass spectrometer (ICPMS). The Si and P contents of the minerals were determined using different digestion methods followed by spectrophotometric analyses (Black et al., 1965; and Bowman, 1988).

Surface charge of minerals is usually examined by two different approaches: ion adsorption and potentiometric titration. The former provides a good measure of ion-exchange capacity at a fixed pH, while potentiometric titration can estimate the change in surface charge with pH. In this study, the cation exchange capacity (CEC) of palygorskite and sepiolite was measured using a BaCl₂ extraction method as described by Hendershot et al. (1993). The changes in surface charge due to pH variations were also examined using the back titration method suggested by Duquette and Hendershot (1993).

3.2.2. Mineralogical characteristics

The mineralogical properties of the minerals were studied by X-ray diffraction (XRD), infrared spectrometry (IR), and electron microscopy. For X-ray diffraction, aliquots from clay samples were saturated with Mg and K using 1 M chloride salts,
followed by washing with distilled water. Oriented mounts were prepared by placing drops of clay aliquot on a glass slide. Analyses by X-ray diffraction were applied on each sample using the following treatents: Mg-saturated air dried, Mg-saturated ethylene glycol solvated, K-saturated air dried, and K-saturated heated at 550°C for 2 h. X-ray diffraction analyses were carried out with a Rigaku XRD diffractometer. Fe-Kα radiation was used with a single crystal (graphite) monochromator. Scans were made at 10° 2θ min⁻¹.

Infrared spectrograms of the minerals were obtained using a Perkin Elmer 983 Ratio Recording Infrared Spectrophotometer. Three mg of clay sample were mixed with 300 mg KBr. The mixture was placed in a 1-cm diameter mold and converted to a pellet under 18,000 psi pressure for 2 min, using a Perkin Elmer Carver Laboratory Press. The pellet was oven dried at 105°C overnight and examined against a blank KBr pellet.

To study the morphology of particles under different treatments, both transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were used. For TEM study, a Philips 300 transmission electron microscope with an acceleration voltage of 100 kV was utilized. The samples were prepared by dispersion and deposition on Cu grids. Specimens of selected samples were also prepared for scanning electron microscopy by fixing aggregates of freeze-dried samples on the sample stubs using cured Spurr resin. The specimens for SEM were examined by a Philips 505 scanning electron microscope.

3.2.3. Purification

The chemical and mineralogical analyses revealed some impurities in the palygorskite and sepiolite samples. Therefore, some acid washing was carried out to purify the samples. They were then homoionized with Ca²⁺ and/or K⁺ and the clay particles with a diameter less than 2 μm were separated using centrifuge sedimentation.
Palygorskites and sepiolites are usually considered to be susceptible to acid decomposition and alteration. However, according to Naghshineh-pour et al. (1989), pre-treatment of palygorskitic soils and a reference clay with pH 5 sodium acetate (NaOAc) buffer, as suggested by Jackson (1979), caused no observable change in the mineralogy as indicated by X-ray diffraction and SEM analyses. Mumpton and Roy (1958) also reported that palygorskite and sepiolite remained unaltered after three months treatment in boiling water at atmospheric pressures. In this study, samples were examined before and after the different purification treatments to elucidate if there were any detectable changes in the chemical and physical structure of minerals. The procedures applied for the purification of palygorskite and sepiolite, as well as homoionization and clay separation, are described below.

3.2.3.1. Palygorskite

Elemental analysis revealed substantial calcium phosphate impurities (>0.3% P) in the palygorskite sample. The TEM study of the original sample also showed small idiomorphic crystals of apatite (Figure 3.1.a). These could interfere with the results of P adsorption/desorption studies. Therefore, acid washing was tried to remove P impurities from palygorskite at pH values of 3, 4, 5, and 7. Five g of original palygorskite were suspended in 500 ml distilled water. The pH of the suspensions was adjusted to a given level by addition of 0.05 M HCl at the rate of 0.05 ml per 10 sec using a Mettler DL21 Titrator. The suspensions were then shaken at room temperature in a rotary shaker for about 24 h and then centrifuged. The supernatant was then decanted and the procedure was repeated seven times. To study the effect of acid washing on removal of P impurities, as well as dissolution of the mineral itself, the concentrations of P and Ca, as well as some clay structural elements such as Si, Al, and Mg, were monitored in the supernatants. The palygorskite suspension was heat-treated in NaOAc, buffered at pH 4 for 3 d. This showed almost the same results as 7 d of acid washing using the HCl pH 4
solution. Therefore, because of its higher feasibility, the NaOAc pH 4 treatment was chosen for the removal of palygorskite P impurities. The NaOAc pH 4 solution was applied using a procedure similar to that of NaOAc pH 5 solution suggested by Jackson (1979), that will be discussed below for sepiolite purification.

3.2.3.2. Sepiolite

Elemental analysis, as well as IR and X-ray patterns of sepiolite, revealed a relatively high quantity of dolomite impurities in the original sepiolite. The crystals of dolomite were also observed under the TEM (Figure 3.1.b). As a carbonate, dolomite may interfere with P adsorption/desorption of sepiolite. Therefore, the original sepiolite needed to be purified initially. To remove the dolomite impurities, clay samples with NaOAc buffered at pH 5 in the ratio of 1 g/100 ml, were heated in a shaking water bath at 60 °C for about 0.5 h. Shaking was continued at room temperature overnight using a rotary shaker. The suspensions were then centrifuged, the supernatant decanted, and the procedure was repeated three times. This was followed by four washings with distilled water to remove the acetate.

3.2.3.3. Homoionization and clay separation

The purified mineral sample was then divided into two parts by weight, which were saturated by either Ca²⁺ or K⁺ using 1 M chloride salts. The mineral sample, using a ratio of 1 g/100 ml of M CaCl₂ or M KCl, was shaken for 24 h and then centrifuged. The supernatant was discarded and the procedure was repeated three times. The homoionized samples were Ca²⁺ and K⁺-saturated palygorskite and sepiolite (Pal-Ca, Pal-K, Sep-Ca, Sep-K). Saturation was followed by washing with distilled water until the chlorine test became negative. The EC of the final supernatant was about 35 μS m⁻¹ for the Ca²⁺-saturated samples and about 42 μS m⁻¹ for K⁺-saturated palygorskite samples. Dispersion of sepiolite took place at about EC of 25 μS m⁻¹ for Ca²⁺-saturated
sepiolite (Sep-Ca) and 30 µS m⁻¹ for K⁺-saturated sepiolite (Sep-K). With respect to
electrolyte concentration, this shows that dispersability of sepiolite is somewhat lower
than that of palygorskite. Following the final centrifugation, the samples were dispersed
in distilled water and the clay fraction was collected by repeated sedimentation and
decantation. The sedimentation time was determined for 2 µm or larger particles utilizing
Stokes Law. The purified, homoionized clay samples were then freeze dried to be
utilized for P adsorption/desorption studies.

3.3. RESULTS AND DISCUSSION

The mineral characteristics and the effects of purification are discussed below.

3.3.1. Palygorskite and sepiolite characteristics

Some of physical, chemical and mineralogical characteristics of original and
purified palygorskite and sepiolite are presented below.

3.3.1.1. Surface area

The results of surface area measurement for the original and treated samples are
given in Table 3.1. Acid washing caused some increase in surface area of both
palygorskite and sepiolite. The main reasons for this are the removal of carbonates with
large particle size and the dispersion of clay colloids. The enrichment of the washed
samples in clay particles is another reason for the larger surface area of the purified
samples compared to the original ones.

Saturation of clay samples with P compounds decreased the surface area, which
is an indication of aggregate formation. This effect was more pronounced in organic
phosphorus inositol hexaphosphate sorption, which shows the higher efficiency of
organic P compounds in clay aggregation over that of inorganic phosphates. The effect
of different treatments on surface area will be discussed in related chapters.
Table 3.1. Surface area of palygorskite and sepiolite after different treatments.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Surface cation</th>
<th>Specific surface area (m² g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>sepiolite</td>
<td>palygorskite</td>
</tr>
<tr>
<td>Untreated mineral</td>
<td>256 ± 10</td>
<td>201 ± 9</td>
</tr>
<tr>
<td>NaOAc pH4</td>
<td>Ca</td>
<td>224 ± 4</td>
</tr>
<tr>
<td>NaOAc pH4</td>
<td>K</td>
<td>222 ± 4</td>
</tr>
<tr>
<td>NaOAc pH5</td>
<td>Ca</td>
<td>396 ± 7</td>
</tr>
<tr>
<td>NaOAc pH5</td>
<td>K</td>
<td>384 ± 7</td>
</tr>
<tr>
<td>Pt⁺-sorbed</td>
<td>Ca</td>
<td>348 ± 6</td>
</tr>
<tr>
<td>Pt⁺-sorbed</td>
<td>K</td>
<td>366 ± 6</td>
</tr>
<tr>
<td>IH⁺⁺-sorbed</td>
<td>Ca</td>
<td>275 ± 3</td>
</tr>
<tr>
<td>IH⁺⁺-sorbed</td>
<td>K</td>
<td>330 ± 3</td>
</tr>
<tr>
<td>Heated at 450°C§</td>
<td>Ca</td>
<td>238 ± 8</td>
</tr>
</tbody>
</table>

† Pi = inorganic phosphate  
‡ IH⁺⁺ = Inositol hexaphosphate  
§ Samples were heated at 450°C for 8 h

3.3.1.2. Elemental analysis

The elemental composition of original and purified palygorskite and sepiolite is presented in Table 3.2. As magnesium silicate clays, both minerals contain a considerable amount of magnesium. The quantity of aluminum in sepiolite is relatively low, while palygorskite contains a substantial amount of this element. Palygorskite and sepiolite are also different with respect to their iron contents. The palygorskite sample contains a considerable amount of iron, while only traces of this element are found in sepiolite. The different elemental compositions may lead to a different affinity of the minerals in sorption/desorption reactions.
Table 3.2. Elemental analyses of original and purified palygorskite and sepiolite samples.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Percent†</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Original Pal†</td>
<td>Pal-pH 4‡</td>
<td>Original Sep§</td>
<td>Sep-pH 5#</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>60.39</td>
<td>61.06</td>
<td>34.99</td>
<td>59.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>10.73</td>
<td>11.15</td>
<td>0.27</td>
<td>0.53</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>10.15</td>
<td>10.62</td>
<td>14.65</td>
<td>24.09</td>
<td></td>
<td></td>
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<tr>
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<td>99.82</td>
<td>100.02</td>
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†Values smaller than 0.01% are presented by --
†Palygorskite PII-1 with no treatment
‡Palygorskite PII-1 treated with NaOAc pH 4
§Sepiolite Eskishehir with no treatment
#Sepiolite Eskishehir treated with NaOAc pH 5

Purification treatments enriched the structural elements, such as Si, Al, Mg, and Fe. This proves the efficiency of the treatments in removal of impurities which seem to
be mostly carbonates. The greater ignition loss at 550-1000 °C for original minerals seems to be related to higher quantities of carbonates in the original samples, a feature that was more pronounced in sepiolite.

Considerable amounts of calcium were found in both palygorskite and sepiolite, even in the purified samples. While this may be due to the presence of lime-containing impurities such as calcite, montmorillonite, or amphiboles, it is also possible that Ca is an essential constituent of these minerals themselves. These findings are in accordance with those of Mumpton and Roy (1958) and Singer (1989).

3.3.1.3. Electron microscopy

Electron micrographs of original and treated palygorskite and sepiolite samples are presented in Figures 3.1 and 3.2. Electron microscopy has shown that palygorskite

![Figure 3.1. The TEM micrographs of the original a) palygorskite and b) sepiolite samples](image)

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consists of bundles of fibers with a length of about 1 μm and a diameter of 10-30 nm; by comparison, with a length of 0.2 μm and diameter of 10 nm, the sepiolite crystals are relatively small. This provides sepiolite with a surface area that is almost twice that of palygorskite. Fibers in the original samples seem to be more flocculated, while crystals of non-silicate constituents exist in the specimens as impurities. The impurities are mostly apatite and carbonate crystals for palygorskite and sepiolite, respectively.

![TEM micrographs of purified samples](image)

**Figure 3.2.** The TEM micrographs of the purified a) palygorskite and b) sepiolite samples

### 3.3.2. Effects of purification on mineral characteristics

To examine the effects of the different treatments applied for removal of impurities, some mineral characteristics were monitored before and after purifications.
3.3.2.1. Purified palygorskite

Acid washing of palygorskite for 4 d at pH 4 reduced the P impurities from 0.95% to less than 0.1% (Table 3.2), while the dissolution of the mineral was less than 0.5%, as calculated on the basis of the amount of Al dissolved (the data for dissolution of the mineral are not shown). At pH 3 the residual P was almost the same; however, the dissolution of palygorskite increased to about 1%. Therefore, as explained earlier, NaOAc 1 N buffered at pH 4 was applied for the removal of palygorskite P impurities.

The pH 4 treated palygorskite was compared with the original sample by means of X-ray diffraction and IR spectroscopy. The results are given in Figures 3.3 and 3.4.

![XRD-patterns of Florida palygorskite (<2μm).](image)

Figure 3.3. The XRD-patterns of Florida palygorskite (<2μm). (A) The original sample (B) NaOAc pH 4 pre-treatment. (D = d-spacing in Å)
Figure 3.4. The IR-patterns of Florida palygorskite ($<2\mu$m). (A) The original sample. (B) NaOAc pH 4 pre-treatment and (C) The differential pattern, A minus B.

The XRD patterns of the original samples showed that, in addition to palygorskite, the reference sample contained a considerable amount of smectite, as indicated by the 14.7 Å peaks for the Mg-saturated clay which expanded to 16.7 Å with ethylene glycol solvation. Also present are quartz, as indicated by the 4.25 Å peak, and a substantial quantity of mica indicated by 3.33 Å peak (Figure 3.3). The palygorskite clay mineral is represented by 10.3, 6.4, 5.4, 4.5, and 3.2 Å peaks. The peaks related to quartz and mica are substantially reduced after clay separation. This shows that quartz
and mica existed mostly as silt sized particles. The phosphate impurities were not detectable by the XRD method.

The IR pattern of palygorskite treated at pH 4 is plotted against that of the original sample in Figure 3.4. As indicated, there were no detectable shifts or changes in the functional groups of this sample due to acid washing of the mineral. The differential line, original minus the treated sample, is also given in Figure 3.4 showing that the IR patterns of the palygorskite were almost the same before and after the acid washing at pH 4, while based on elemental analysis data (Table 3.2), the P impurities were substantially reduced after purification. Therefore, the treated sample seems to be an acceptable one for the adsorption/desorption studies.

3.3.2.2. Purified sepiolite

The IR patterns of the sepiolite sample, before and after acid washing using NaOAc pH 5, is given in Figure 3.5. The differential pattern, original minus treated sample, is also presented in the same Figure. The differential pattern is similar to the IR pattern of dolomite that was illustrated by Kodama (1985). This shows that the major impurity in the sepiolite sample is dolomite, that was removed by NaOAc pH 5 as suggested by Jackson (1979). Since NaOAc pH 5 is also a safe treatment (Naghshineh-pour et al., 1989), the treated clay sample maintains its original sorption/desorption characteristics.
Figure 3.5. The IR-patterns of Eskishehir sepiolite (<2μm). (A) The original sample, (B) NaOAc pH 5 pre-treatment, and (C) the differential pattern, A minus B.
3.4. CONCLUSIONS

To understand the behavior of a mineral in sorption/desorption reactions, a
detailed characterization of the mineral is required. In this study an intensive physico-
chemical analysis, as well as mineralogical studies on palygorskite and sepiolite, were
carried out. The results showed that purified sepiolite possesses a larger surface area due
to its smaller crystal size as revealed by electron microscopy.

Both palygorskite and sepiolite contain relatively high amounts of magnesium.
Palygorskite also contains a considerable content of Al and Fe, while only trace amounts
of these elements were found in sepiolite. About 2% of CaO were found in palygorskite
and sepiolite even after purification. This may be explained by the close association of
these minerals with carbonates or some other silicates such as smectite or amphiboles, as
discussed in the literature (Mumpton and Roy, 1958; Singer, 1989).

The purification treatments effectively removed the phosphate and carbonate
impurities as revealed by physico-chemical analyses, while there were no detectable
shifts in the clay structure. Acid washing removed P impurities, and clay separation
enriched the palygorskite sample by removal of quartz and mica particles. The sepiolite
sample was also enriched by removal of dolomite impurities using NaOAc buffered at
pH 5.
CHAPTER 4
ADSORPTION ISOTHERMS AND DESORPTION OF PHOSPHATE BY PALYGORSKITE AND SEPIOLITE

4.1. INTRODUCTION

Interactions of the major forms of phosphorus with soil constituents are important with respect to the interpretation and prediction of fertilizer and environmental aspects of phosphorus in soils. A large body of information is now available regarding characterization and understanding the interaction mechanisms between soil constituents and phosphorus compounds. However, quantitative information on the P adsorption/desorption of palygorskite and sepiolite is limited. The main objective of this part of the research was to study the adsorption isotherms, as well as desorption of two P compounds, by the two previously discussed clay samples at different levels of electrolyte concentration.

4.2. MATERIALS AND METHODS

Adsorption isotherms, and desorption of sorbed orthophosphate (Pi) and inositol hexaphosphate (IHP) on palygorskite and sepiolite, were examined under different conditions of surface cation and electrical conductivity (EC). The possibility of phosphate sorption on intra-crystalline channels of the minerals was also investigated in this study.
4.2.1. Clay suspension

The homoionized clay samples used for this study were: sepiolite Ca\textsuperscript{2+}-saturated (Sep-Ca), sepiolite K\textsuperscript{+}-saturated (Sep-K), palygorskite Ca\textsuperscript{2+}-saturated (Pal-Ca), and palygorskite K\textsuperscript{+}-saturated (Pal-K). A 6.25 g sample of each homoionic clay was suspended in about 450 ml deionized water in a 500 ml volumetric flask. For dispersion of aggregates, the suspension was being stirred overnight using a magnetic stirrer. The initial pH of the suspensions were 8.8 and 8.5 for Sep-K and Sep-Ca, respectively. The pH was 7.5 and 7.0 for Pal-K and Pal-Ca.

Before the P adsorption experiment the volume of suspension was increased to 500 ml while its EC and pH were adjusted using 0.1 M KCl and 0.05 M HCl or NaOH. The final EC of suspensions were 1, 4, 10, and 20 dS m\textsuperscript{-1}. The addition of salt decreased the pH of the suspensions for all clay samples. This could be the due to exchange of adsorbed protons by the added cation, or an increase in the specific adsorption of OH\textsuperscript{-} by the clay surfaces. The pH of all suspensions was adjusted to 7.0. The EC of suspensions was measured using a CDM 83 electrical conductivity meter equipped with a CDC 114 pipette cell. To adjust the pH of suspensions, 0.05 M HCl or NaOH were added at a rate of 0.05 ml per 10 sec using a Mettler DL21 titrator. One ml of chloroform was added to suppress microbial activity.

4.2.2. P compounds

For this study, sodium salts of orthophosphate (Pi) (Fisher, ACS) and inositol hexaphosphate (IHP) (BDH) were used as inorganic phosphate and organic phosphate, respectively. The phosphorus contents of all phosphates studied were determined experimentally. The organic P was digested by acidified ammonium persulphate oxidation (Bowman, 1989). Orthophosphate was determined by a colorimetric method (Murphy and Riley, 1962). The stock solutions of organic phosphates were prepared with autoclaved deionized distilled water and stored in autoclaved containers under
refrigeration. The hydrolysis of organic phosphates in stock solutions was tested by measuring the inorganic phosphate level before each use.

4.2.3. P adsorption experiment

A 10 ml clay suspension adjusted to a given EC and pH 7.0, and containing 125 mg clay was added to a 50-ml polypropylene screw-cap centrifuge tube. A 15 ml KCl solution with the same pH and EC as the clay suspension, and a given concentration of either Pi or IHP, was also added to the tube. Concentrations of P in the 25 ml suspension for Pi adsorption experiments were: 0.00, 0.06, 0.16, 0.32, 0.64, 1.28, and 2.00 mM. For the IHP adsorption experiment concentrations of 0.00, 0.06, 0.16, 0.32, 1.00, 2.00, 3.00, 6.50, and 10.0 mM were applied. Suspensions were shaken horizontally for 24 h. The experiments were conducted at a constant temperature of 25±0.1°C in an agitated water bath. The suspensions were centrifuged at 20,000 g and the concentration of P was determined in the supernatant. Each treatment was duplicated. Phosphorus was determined by the ascorbic acid method (Murphy and Riley, 1962), the absorbance being read at 720 nm using a Beckman Model DU Spectrophotometer. The reproducibility of the concentration data was ±4%. The P in the supernatant was considered as the equilibrium P concentration, and the adsorbed P was calculated based on the difference between the initial and equilibrium P concentration of solution. The adsorbed P was expressed as cmol kg⁻¹.

4.2.4. P desorption experiment

At the end of the adsorption period, the centrifuge tubes containing clay and P solution were weighed. The suspensions were centrifuged, supernatant taken for P measurement, and the tubes containing the sedimented clay were weighed. A given amount of KCl electrolyte adjusted at the previous levels of EC (1, 4, 10, and 20 dS
and pH (7.0) for each tube was added to the sediments to provide 25 ml of suspension. The amount of electrolyte was calculated by taking the difference between the weight of each tube before and after withdrawing the supernatant. The electrolytes were free of phosphate. Using a Smi 2600 multi-tube vortexer, the clay particles sedimented in the tubes were brought into the suspension. The clay content of the suspensions was 0.5%, the same as in P adsorption experiment. Suspensions were shaken horizontally for 24 h at a constant temperature of 25± 0.1°C in an agitated water bath. The suspensions were centrifuged and the concentration of P in the supernatant was determined by the method described above. The concentration of phosphorus was corrected for the solution P left in the sediment and the desorbed P was calculated as cmol kg⁻¹.

4.2.5. P adsorption isotherms

To describe the relationship between the amount of phosphate in the adsorbed phase and in solution, Freundlich, Langmuir and a modified Langmuir (Muljadi et al., 1966) equation were fitted to the experimental isotherm data. The three equations were previously discussed in Chapter 2. Using the SAS computer program (SAS Institute, 1985), the adsorption data were incorporated in the equations and different parameters of each model were calculated. The degree of fit of the data was evaluated based on R² (determination coefficient) and F values.

4.3. RESULTS AND DISCUSSION

The adsorption isotherm of orthophosphate on Sep-Ca at EC = 4 dS m⁻¹ and pH 7.0 is given in Figure 4.1 a, b, and c. The performance of the adsorption model should be evaluated from a practical and a statistical point of view. Practically, the models simulated the data points reasonably well, however, the modified Langmuir shows a closer estimate of the actual values (Figure 4.1.c).
All three models are empirical but they have the advantage of being simple with respect to P solution concentration. Statistically the models are also acceptable. The $F$ and $p$ values indicate that the predictability of the models is acceptable at the 95% confidence interval. However, among the three models, the modified Langmuir model showed the best fit for the experimental data, showing the highest $R^2$ and $F$ values, and acceptable predictability at the 99.99% confidence interval.

Figure 4.1. a) Freundlich, b) Langmuir, and c) modified Langmuir plotting of Pi adsorption isotherm by Sep-Ca at $EC = 4$ dS m$^{-1}$ and $pH = 7$. 

[Graphs showing data for each model with equations and values for $R^2$, $F$, and $p$.]
The three models were examined for the entire adsorption isotherms data set and in almost all cases, the modified Langmuir model provided the best fit to the experimental data; therefore, all isotherms were plotted using this model.

4.3.1. Orthophosphate adsorption/desorption of sepiolite

In the following section, the adsorption isotherms and desorption of adsorbed Pi on Ca- and K-saturated sepiolite samples at different electrolyte conditions are discussed.

4.3.1.1. Orthophosphate adsorption isotherms of sepiolite

Inorganic P adsorption isotherms of Sep-Ca and Sep-K at different EC are shown in Figures 4.2 and 4.3. The amount of adsorbed P increases with increasing EC and reaches its maximum at EC of 20 dS m\(^{-1}\). The increase in Pi adsorption is largest between EC values of 1 and 4 dS m\(^{-1}\). An increase of P adsorption due to increase in

![Graph showing orthophosphate adsorption isotherms of Sep-Ca at different EC levels.](image)

Figure 4.2. Orthophosphate adsorption isotherms of Sep-Ca at different EC levels.
electrolyte concentration has been also reported for other clay minerals (Bar-Yosef et al., 1988).

The adsorption maxima in Ca-saturated sepiolite is higher than that of K-sepiolite. Figure 4.4 shows the adsorption isotherms of Sep-Ca and Sep-K at two different EC levels. At lower EC the effect of surface cation is more pronounced, and the amount of P adsorption on the clay surface saturated with Ca is higher than that of K-saturated surface. The maximum P adsorption by Ca-sepiolite at EC = 4 and pH 7.0 is about 0.7 cmol kg⁻¹, which is comparable with the P adsorption capacity of Ca-kaolinite and montmorillonite reported by Bar-Yosef et al. (1988). Considering the lower pH of

![Figure 4.3. Orthophosphate adsorption isotherms of Sep-K at different EC levels.](image)

the adsorption media in the Bar-Yosef's experiment, one may conclude that sepiolite has a higher Pi adsorption capacity than montmorillonite and other crystalline silicate clay minerals. This may be due to the larger external surface area of sepiolite and its high dispersability at relatively high electrolyte concentrations.
4.3.1.2. Effect of EC and surface cation on P adsorption

The EC of the electrolyte and the valence of surface cations positively affect the

![Graph showing Sorbed P (cmol/kg) vs Equilibrium P concentration (mM)]

Figure 4.4. Orthophosphate adsorption isotherms of Sep-Ca and Sep-K at two different EC levels.

Pi adsorption. In different studies it has been shown that Ie of electrolyte and the type of exchangeable cation play an important role in determining P adsorption by silicate clay minerals. Pissarides et al. (1986) found that elevated Ie and exchangeable Ca, rather than K, decreased the P concentration in the solution phase of kaolinite and montmorillonite. Bowden et al. (1980) explained the effect of Ie on P adsorption by the effect of ionic strength on the charge density of the diffuse double layer that counters the charge on P-adsorbing surfaces. Using a similar explanation, Kafkafi et al. (1988) clarified that such an effect may be the influence of Ie on the extent of DDL on clay planar faces.

Increased Ie restricts the extent of the DDL and consequently reduces the masking of P adsorption sites on clay edges by the negative electric field of clay faces. This
mechanism accords with the fact that higher P adsorption was obtained when Ca, rather than K, was the exchangeable cation. A similar effect of Ie and exchangeable cation on anion adsorption by montmorillonite and kaolinite was obtained for other anions such as borate (Keren and O'Connor, 1982). This hypothesis may also explain the different response of the sepiolite sample at different EC levels.

At lower EC, especially in K-saturated sepiolite samples, a large number of adsorption sites are masked by the negative electric field of the clay colloids. Therefore, any increase in EC or consequently Ie of electrolyte may significantly enhance the number of available sites for P adsorption. However, as more adsorption sites become available by increased EC or the presence of divalent rather than monovalent surface cations, the number of adsorption sites becomes a limiting factor at a constant pH and further elevation of EC may not significantly increase the P adsorption capacity of the mineral.

At higher EC values, due to the relatively high concentration of KCl electrolyte (about 0.15 M at EC of 20 dS m⁻¹), some of the surface-Ca²⁺ ions may be exchanged by the K⁺ ions. This, in turn, would decrease the positive effect of Ca²⁺ on sorption capacity of the mineral causing a relatively similar Pi sorption behavior for Sep-Ca and Sep-K at EC of 20 dS m⁻¹ (Figure 4.4).

Traina et al. (1986) reported that increasing Ie decreased residual orthophosphate solubility in acidic (pH = 5.5) montmorillonitic soil containing exchangeable Al. They attributed the effect of Ie to displacement of exchangeable Al³⁺ by the electrolyte cation, and subsequent precipitation of P as Al(OH)₂H₂PO₄(s). Despite the similar effect of Ie on P adsorption in this study, the effect of exchangeable Al³⁺ may be ruled out due to the relatively high pH (7.0) of clay suspension. However, in this case Ca²⁺ may precipitate solution P to form calcium phosphates.
4.3.1.3. Orthophosphate desorption of sepiolite

The results of the desorption experiment showed that the adsorbed orthophosphate can be released easily. Desorption took place in an electrolyte with the same EC and pH as that during the adsorption reaction. In Figures 4.5 and 4.6, the amount of released Pi is correlated with the amount of sorbed Pi, for both Ca$^{2+}$ and K$^+$ surface cations. Having an intercept of almost zero and a slope of close to unity, a straight line represents the Pi adsorption and desorption relationship of sepiolite. Based on these Figures, one may conclude that all Pi molecules sorbed at a given EC and pH can be released under the same conditions, if the solution Pi is depleted.

The elemental analyses (Chapter 3), as well as chemical structure of sepiolite (Chapter 2), indicate that the edge positions in the octahedral structures of sepiolite are filled predominantly with Mg$^{2+}$. Magnesium exerts a rather weak preference for phosphate ions compared to Ca, Fe, and Al. With respect to phosphate adsorption,

\[ Y = 0.004 + 1.009 X \]

\[ R^2 = 0.998 \]

Figure 4.5. Desorption of sorbed Pi from Sep-Ca
Figure 4.6. Desorption of sorbed Pi from Sep-K

therefore, sepiolite may act as an inert mineral. Therefore, it may be concluded that, due
to its high surface area and high dispersability, sepiolite adsorbs substantial quantities of
phosphate from a solution with high concentration of this anion. The adsorbed P,
however, may be released upon depletion of solution in phosphorus. Considering the Pi
adsorption/desorption behavior of sepiolite, this mineral might be utilized as a carrier for
orthophosphate compounds.

Sepiolite might be also used as a cleaning agent for Pi-contaminated solutions.
Having a high adsorption capacity, a column filled with sepiolite, seems to sorb Pi from
a Pi-contaminated solution passing through. The sorbed Pi can then be washed away by
passing a phosphate-free electrolyte (e.g., ordinary water) through the column. The
column may be reused after washing.
4.3.2. Orthophosphate adsorption/desorption of palygorskite

In this part, the adsorption isotherms and desorption of sorbed Pi on Ca- and K-saturated palygorskite samples under different electrolyte conditions are discussed.

4.3.2.1. Orthophosphate adsorption isotherms of palygorskite

Orthophosphate adsorption isotherms of palygorskite can also be well described using the modified Langmuir equation. Figures 4.7 and 4.8 represent the Pi adsorption isotherms of Pal-Ca and Pal-K at pH 7 and different EC. The Pi adsorption maxima increase with EC, and at lower EC the effect of elevated electrolyte concentration is more pronounced. The adsorption maxima of Pal-Ca is somewhat higher than that of Pal-K especially at EC < 20 dS m⁻¹. These observations may be explained by considering the

![Graph showing orthophosphate adsorption isotherms](image.png)

**Figure 4.7. Orthophosphate adsorption isotherms of Pal-Ca at different EC levels**
effect of ionic strength of the electrolyte and the valence of exchangeable cation, as previously discussed. The adsorption maximum of Pal-Ca at pH 7 and EC = 4 dS m\(^{-1}\) is about 1.2 cmol phosphorus per kilogram of clay, which exceeds the adsorption capacity of sepiolite at the same conditions by almost 2 times. The chemical analysis of palygorskite (Table 3.2) revealed that palygorskite contains substantial amounts of aluminum. Having a high affinity for phosphate anions, Al atoms seem to provide energetic sites for phosphate adsorption. This may explain the higher Pi adsorption capacity of this mineral over sepiolite despite its smaller surface area.

![Graph](image)

Figure 4.8. Orthophosphate adsorption isotherms of Pal-K at different EC levels.

4.3.2.2. Orthophosphate desorption of palygorskite

Desorption of adsorbed orthophosphate from palygorskite is examined in an electrolyte with the same conditions of EC and pH as employed during the adsorption reaction. The relationship between sorbed and released Pi for both Ca\(^{2+}\) and K\(^{+}\) surface cations is presented in Figure 4.9. The release of sorbed Pi from palygorskite is lower
than what was adsorbed, contrary to the P desorption for sepiolite. As shown in Figure 4.9, about one fifth to one third of sorbed Pi may be released.

The chemical structure of palygorskite gives this mineral a relatively high Pi retention capacity. The Al atoms located at the octahedral positions strongly bond the sorbed phosphate and restrain its release into the solution. The desorption of sorbed orthophosphate from Pal-K is somewhat higher than that of Pal-Ca. This might be due to the effect of Ca$^{2+}$ on the diffuse double layer. Ca$^{2+}$ restricts the extent of DDL, providing a closer approach of the phosphate anions to the adsorption sites. As a result, in Pal-Ca the sorbed phosphate is being retained by the surface more intimately than in Pal-K. Also, due to its higher charge density, Ca$^{2+}$ may attach the phosphate anion to the colloid surface as a bridge cation more strongly than K$^{+}$ does. In the case of Pal-Ca, the precipitation of Ca-phosphate also can not be ruled out and may decrease the released phosphate. Considering the Pi desorption behavior of palygorskite, it might be concluded that application of potassium fertilizers increases the availability of fixed phosphate by clay minerals in palygorskite-dominated soils.

![Figure 4.9. Desorption of sorbed Pi from Pal-Ca and Pal-K](image-url)
4.3.3. Inositol hexaphosphate adsorption/desorption on sepiolite

The adsorption isotherms and desorption of adsorbed IHP on Ca- and K-saturated sepiolite samples under different electrolyte conditions are discussed below.

4.3.3.1. Inositol hexaphosphate adsorption isotherms of sepiolite

The inositol hexaphosphate (IHP) adsorption isotherms of sepiolite can be plotted satisfactorily using the modified Langmuir equation. Figure 4.10 and 4.11 show the IHP adsorption isotherms of Sep-Ca and Sep-K at pH 7 and different EC. The adsorption maxima are increased with the EC of electrolyte; however, the increase is much sharper from EC 1 to 4 than from EC 4 to 20 dS m⁻¹. The Ca²⁺-saturated mineral showed a slightly higher adsorption maximum than the K⁺-saturated mineral at lower EC. In

![Figure 4.10. Inositol hexaphosphate adsorption isotherms of Sep-Ca at different EC levels.](image-url)
comparison with orthophosphate adsorption, IHP is adsorbed in much higher quantities. For Sep-Ca at pH 7 and EC = 4 dS m\(^{-1}\), the adsorption maxima of IHP is about 24 cmol kg\(^{-1}\), while that of Pi was only 0.7 cmol kg\(^{-1}\). It seems that the IHP adsorption capacity of sepiolite exceeds the adsorption maxima of Pi by more than 30 times. Having more phosphate groups, IHP shows a higher chemical affinity for the surface.

Due to their large size, organic molecules may display several adsorption phenomena. These include the "octopus" effect and metal bridging mechanisms. High molecular weight organics with multiple ionizable functional groups often have high adsorption affinities that are at best only weakly affected by competitive anions (e.g., Cl\(^-\) or HCO\(_3^-\)). Podoll et al. (1987) attributed the strong adsorption of polymers to an "octopus" effect. Adsorption of organic molecules (OM) to clay particles through a polyvalent cation link (or bridge) is also a common occurrence. Based on infrared

![Figure 4.11. Inositol hexaphosphate adsorption isotherms of Sep-K at different EC levels.](image-url)

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absorption studies, Mortland (1970) explained that due to the lowering of the OH stretching frequencies of water resulting from the H-bond formation, the adsorption mechanism should include a water bridge, namely clay-metal-H$_2$O-OM, particularly for cations of high adsorption energy.

The P-group in the organic phosphates (IHP) is the functional group capable of specifically binding with a metal atom on the adsorbent surface and therefore, the number of P-groups per molecule of an organic phosphate would partially determine the affinity of the phosphate molecule to the surface sites. The functionality of multiple P groups of IHP may lead to the formation of a more stable complex with metal atoms on the surface, favoring the adsorption. Furthermore, high charge density of IHP ions makes it easier to approach the surface through electrostatic attraction, even though this contribution may be weak (Hansmann and Anderson, 1985). These factors may explain the strong adsorption of IHP by the minerals.

4.3.3.2. Inositol hexaphosphate desorption of sepiolite

The desorption of IHP from Ca-saturated sepiolite is presented in Figure 4.12. It seems that at lower levels of adsorbed P, the desorption is negligible. The relatively large size and the high number of functional groups of the IHP molecules may explain its behavior. The larger a molecule, the greater their number of segments (functional groups) that will attach to the surface, and the more difficult it becomes to desorb the molecule. The competitive nature of other aqueous anions may affect the total number of attached segments. However, unless all the segments are desorbed, the oligomer will remain adsorbed with each of its desorbed functional groups always relatively close to the surface for competitive re-adsorption (Hansmann and Anderson, 1985).

Based on the trend represented on Figure 4.12, when adsorption passes a certain level, about 15 cmol kg$^{-1}$, the desorption increases exponentially. This shows that after a given degree of surface coverage, the energy of IHP adsorption to the surface decreases
substantially. Figure 4.13 shows the quantitative desorption of IHP form Sep-Ca and Sep-K. The pattern reveals a slightly higher desorption from Sep-Ca. Therefore, one may conclude that, since IHP adsorption of Sep-Ca is slightly higher than that of Sep-K, the degree of release may also be higher. The IHP ions are much larger in size compared to orthophosphates and are multiple charged. The valence of exchangeable cation, therefore, seems to play no significant role in retention of the anions on the surface. The degree of desorption is likely governed by the amount of adsorbed phosphate as a main factor.

4.3.4. Inositol hexaphosphate adsorption/desorption of palygorskite

In this part, the adsorption isotherms and desorption of adsorbed IHP on Ca- and K- saturated palygorskite under different electrolyte conditions are discussed.
4.3.4.1. Inositol hexaphosphate adsorption isotherms of palygorskite

The IHP adsorption isotherms of Pal-Ca and Pal-K at pH 7 and different EC are presented in Figures 4.14 and 4.15. The adsorption maxima increase sharply when EC increased from 1 to 4 dS m⁻¹ and a further increase in EC seems to have a mild effect on IHP adsorption. This shows that at lower EC (1 dS m⁻¹) the extent of the diffuse double layer and the repulsion of the anion by the negative electric field of clay faces are major factors limiting the approach of the anions to the surface. However, a relatively small increase in EC is sufficient for large and polydentate IHP molecules to overcome the repulsion and saturate the colloid surfaces.

Compared with orthophosphate adsorption, EC seems to have a more significant role in IHP adsorption by palygorskite. The adsorption maxima at EC = 4 dS m⁻¹ is about twice that at EC = 1 dS m⁻¹. This behavior of palygorskite may have some useful
applications. For example in a saline system in which the electrolyte concentration changes drastically due to irrigation, a reduction of electrolyte EC from 4 to 1 dS m\(^{-1}\) would reduce the adsorption capacity of palygorskite to half as much. This phenomenon might favor the availability of sorbed IHP on soils with palygorskite.

In contrast to Pi adsorption, the IHP adsorption capacity of palygorskite is smaller than that of sepiolite. However, palygorskite contains substantial amounts of structural Al. The large size, as well as the high charge density of IHP molecules, seem to overcome the difference between the P sorption affinity of Mg\(^{2+}\) and Al\(^{3+}\) as octahedral cations. Thus, even the lower affinity of Mg\(^{2+}\), as clay structural cations, to adsorb IHP molecules is enough to saturate almost all adsorption sites of colloids. In this case, however, the specific surface area is likely the limiting factor. The larger the specific surface area, the higher can be the quantity of adsorbed IHP.

Figure 4.14. Inositol hexaphosphate adsorption isotherms of Pal-Ca at different EC
At the EC of 4 dS m$^{-1}$ the IHP sorption of Ca-saturated palygorskite reached to $0.62 \mu$mol m$^{-2}$ compared to that of sepiolite, which amounted at $0.64 \mu$mol m$^{-2}$. This shows that the palygorskite and sepiolite samples possess almost the same surface densities of IHP sorption sites and the larger surface area of sepiolite as a major factor induced the higher IHP sorption capacity of this mineral over that of palygorskite.

Considering the chemical structure of palygorskite and sepiolite, silanol (Si-OH) groups are associated in large numbers with terminal Si tetrahedra. At the external surfaces, broken Si-O-Si bonds compensate their residual charge by accepting H$^+$ or (OH$^-$) and become Si-OH groups. The abundance of these groups is related to the dimensions of the fibers and crystal imperfections. In palygorskite these groups are less abundant than in sepiolite. The Si-OH groups may interact with molecules adsorbed on external surfaces, particularly with organic constituents.

![Graph showing Inositol hexaphosphate adsorption isotherms of Pal-K at different EC](image)

**Figure 4.15.** Inositol hexaphosphate adsorption isotherms of Pal-K at different EC
4.3.4.2. Inositol hexaphosphate desorption of palygorskite

The desorption of sorbed IHP from palygorskite, as presented in Figure 4.16, follows the same pattern as sepiolite. At lower levels of adsorbed IHP, the desorption is negligible, but as adsorption exceeds a given level, the desorption increases drastically. The desorption of IHP from Pal-Ca and Pal-K shows the same pattern. As was discussed for the sepiolite, the valence of the exchangeable cation seems to play no significant role in the retention of IHP on the clay surfaces and the quantity of adsorbed IHP governs the release of this anion from the sorbed phase. Desorption of adsorbed IHP on Pal-Ca seems to exceed that of Sep-Ca. This is likely to be due to the smaller number of Si-OH groups for Pal-Ca and lower retention capacity of this mineral.

Figure 4.16. Desorption of sorbed IHP from Pal-Ca and Pal-K
4.3.5. Adsorption of phosphate by heated clay samples

As indicated in the chemical structure of sepiolite and palygorskite (Chapter 2), there are intra-crystalline channels in the fibrous structure of these clay minerals. Normally these spaces are filled with hydration and zeolitic water. The contribution of these channels to adsorption processes has been reported by several researchers (Serna and Van Scoyoc, 1979; Dandy and Nadiye-Tabbiruka, 1982; Shuali et al., 1988). To investigate the role of the structural channels in adsorption of phosphate molecules, heated samples (450°C for 8 h) of sepiolite and palygorskite were examined. According to Rodriguez Reinoso et al. (1981), the heat treatment removes both zeolitic and coordinated (Chapter 2) types of H₂O molecules from the channels and results in irreversible collapse of the channel structure. The heated clay samples were then examined for P adsorption at pH 7 and EC = 4 dS m⁻¹ following the procedure explained before.

The results of this experiment are summarized in Figure 4.17 (the results are presented for sepiolite only). The heat treatment reduces the specific surface area for both sepiolite and palygorskite clays. The adsorption of orthophosphate was reduced after heating the clay samples. This likely means that the channels are partly involved in the P adsorption, and after they had collapsed some of the adsorption sites were no longer available to the phosphate molecules. The heat treatment did not decrease the IHP adsorption capacity of the minerals, instead, there seems to be a slight increase in IHP adsorption. Based on this observation, one may conclude that the intra-crystalline openings do not provide adsorption sites to the IHP molecules. In this regard, the physical size of the channel might be the limiting factor. According to Rodriguez Reinoso et al. (1981), the heat treatment destroys the intra-crystalline channels with a diameter of less than 10 Å. This likely creates some new, large openings with diameter of up to

69
about 50 Å. Although, the new openings do not compensate for the decreased BET surface area, they may provide some new adsorption sites for IHP groups.

![Graph showing IHP and SSA for normal and heated conditions.](image)

**Figure 4.17. Effect of heat treatment on P adsorption properties of sepiolite**

4.4. CONCLUSIONS

In this study, the adsorption/desorption of orthophosphate as an inorganic phosphate (Pi) and inositol hexaphosphate (IHP) as an organic phosphate on palygorskite and sepiolite were examined. The sorption isotherms of both Pi and IHP on the minerals followed a modified Langmuir isotherm, while EC of electrolyte and the valence of the surface cation positively affected the Pi sorption capacity of the minerals. At EC of 4 dS m⁻¹ the Pi sorption of sepiolite and palygorskite reached about 0.7 and 1.2 cmol kg⁻¹ which seems to be higher than sorption capacities reported for other crystalline silicate clay minerals.

The sorbed Pi on sepiolite was easily desorbed upon phosphate depletion of electrolyte. This may be due to the abundance of Mg atoms in octahedral positions in the
crystal structure, inducing a low affinity for phosphate retention. Considering the Pi sorption/desorption behavior of sepiolite, this mineral may be introduced as a carrier for orthophosphate compounds. It may also be a good cleaning material for orthophosphate contaminated waters.

Palygorskite possesses a higher content of structural Al atoms, and showed a higher Pi sorption capacity than sepiolite. The sorbed phosphate was not as easily desorbable as that of sepiolite. Palygorskite saturated with K+ as a surface cation showed higher desorption over the Ca2+-saturated mineral. Therefore, it may be concluded that application of potassium in palygorskitic soils would increase the availability of sorbed phosphates.

The IHP sorption capacity of the minerals exceeded the Pi sorption capacities by several times. The large number of functional groups and higher charge density of IHP molecules may explain the higher affinity of this compound for surface sorption sites. Increased EC at lower levels of electrolyte concentration sharply increased the IHP sorption of the minerals, while the surface cations only slightly affected the sorption capacity of the minerals. The sorbed IHP at lower levels of sorption was hardly desorbable, however, as the amount of sorbed IHP passed a certain level, desorption increased sharply. This may be explained by the high affinity of the surface for the first layer of sorbed molecules and reduction of sorption energy for the sequential layers of sorbate that accumulated on the clay surfaces.

The IHP sorption capacity of sepiolite exceeded that of palygorskite, while the surface sorption site densities were almost the same for the minerals. Therefore, it is concluded that the higher IHP sorption capacity of sepiolite is mainly attributed to its larger surface area over that of palygorskite.

Heat treatment at 450 °C reduced the BET surface area of palygorskite and sepiolite. It also decreased the Pi sorption capacity of the minerals, showing that sorption
of Pi molecules may partially take place in crystalline channels of palygorskite and sepiolite.

The IHP sorption capacity of minerals slightly increased after the heat treatment, suggesting that the structural channels are not available for the adsorption of large IHP molecules. The slight increase in sorption of IHP molecules with heat treatment, may be due to creation of new, larger openings in the mineral structure.
CHAPTER 5
KINETICS OF PHOSPHATE ADSORPTION BY
PALLYGORSKITE AND SEPIOLITE

5.1. INTRODUCTION

Due to the widespread occurrence of phosphate deficiency and the complex nature of the problem, the reaction between phosphate and soil components is one of the most frequently studied subjects in soil science; however, data on the specific interactions of phosphate with palygorskite and sepiolite is meager. Phosphate sorption isotherms of palygorskite and sepiolite under different conditions of surface cation and electrical conductivity (EC) of solution were discussed in Chapter 4. This chapter addresses the kinetics of both organic and inorganic phosphate sorption of palygorskite and sepiolite under different pH conditions. Kinetic modeling and the role of the surface cation and charge characteristics of the minerals on P sorption kinetics are also discussed in this part.

Kinetics of reactions in soil and aquatic environments are of extreme importance and interest. Most of the chemical processes that occur in these systems are dynamic, and a knowledge of the mechanisms and kinetics of these reactions is fundamental. Moreover, to understand properly the fate of applied fertilizers, pesticides, and organic pollutants in soil with time, and to thus, improve nutrient availability and the quality of our ground water, one must study kinetics.

The objective of this part of the work was to study the P sorption of palygorskite and sepiolite with an emphasis on the following aspects:
i) The kinetics of organic and inorganic P sorption by Ca$^{2+}$ and K$^+$ saturated palygorskite and sepiolite.

ii) The effect of pH on P partitioning between solid and liquid phases at constant ionic strength and quantity of P in the system.

The further elucidation of P behavior in the presence of clay minerals predominant in soils could help in improving P management under field conditions where the P forms change rapidly.

5.2. MATERIALS AND METHODS

In this part of the study, the kinetics of phosphate sorption by palygorskite and sepiolite under different conditions of surface cations and electrolyte pH were investigated.

5.2.1. Clay minerals

The clay minerals examined in this experiment were; 1. palygorskite PFI-1, from the CMS repository source, and 2. a geological sample of sepiolite obtained from Eskishehir, Turkey. To remove the phosphate impurities, the palygorskite sample was treated with Na-OAc buffered at pH 4, as explained in Chapter 3. The sepiolite sample was treated with Na-OAc pH 5 (Jackson, 1979) to remove carbonatic impurities. The purified clays (< 2μm) were then homoionized with 1 N CaCl$_2$ or KCl followed by freeze-drying. The homoionized clay samples used for this study were: sepiolite Ca$^{2+}$-saturated (Sep-Ca), sepiolite K$^+$-saturated (Sep-K), palygorskite Ca$^{2+}$-saturated (Pal-Ca), and palygorskite K$^+$-saturated (Pal-K).

5.2.2. P compounds

Sodium salts of orthophosphate (Pi) (Fisher, ACS) and inositol hexaphosphate (IHP) (BDH) were used in this study. The phosphorus contents of all phosphates studied
were determined experimentally. The organic P was digested by acidified ammonium persulphate oxidation (Bowman, 1989). Orthophosphate was determined by a colorimetric method (Murphy and Riley, 1962). The stock solutions of organic phosphates were prepared with autoclaved deionized distilled water and stored in autoclaved containers under refrigeration. The hydrolysis of organic phosphates in stock solutions was tested by measuring inorganic phosphate level of the solution each time before use.

5.2.3. Electrolyte conditions

A 5 g sample of each clay was stirred with 500 ml distilled water in a 1 L Nalgene centrifuge container for 24 hr at room temperature. The EC and pH of suspensions were 37 μS m⁻¹ and 6.9 for Pal-Ca, 45 μS m⁻¹ and 7.5 for Pal-K, 30 μS m⁻¹ and 8.5 for Sep-Ca, and 35 μS m⁻¹ and 8.7 for Sep-K. The EC was adjusted at 4 dS m⁻¹, using 1 M KCl solution, while the volume of suspension increased to 900 ml. The addition of salt to the clay suspension decreased the pH of the suspension for all clay samples. This could be the effect of exchanging adsorbed protons by the added cation and/or an increase in the specific adsorption of OH⁻ by the surface. The pH of suspensions was adjusted to 6, 7, and 8 by adding 0.05 M HCl or NaOH at the rate of 0.05 ml per 10 s using a Mettler DL21 titrator. An aliquot of 18 ml was withdrawn from each suspension and increased to 20 ml using KCl solution adjusted at the same EC and pH of clay suspension. This was considered as a blank to quantify the release of OH⁻ during the P sorption reaction.

While the clay suspension was being strongly stirred, 100 ml of P solution adjusted at the same EC and pH was added. The initial concentration of P in the suspensions were 0.65 and 1.95 mM for the Pi and IHP treatments respectively. The P concentrations had been selected based on the results of P sorption isotherms (Chapter 4) at which maximum adsorption took place. The concentration of KCl was 0.031 M, and
the clay content was 5 mg ml⁻¹. Two replicates of 6 ml suspension were taken using two connected pipettes at 2, 5, 10, 30, and 60 min after the P addition, and immediately filtered through a Millipore membrane (0.025 μm pore size) using a Buchner funnel connected to the laboratory vacuum system. After 1 h, 1 ml chloroform was added to each container and the containers were capped and placed in a rotary shaker.

Additional withdrawals of suspension were carried out after 2, 4, 8, 16, 24, 48, 72, 96, 120 and 168 h of reaction. Samples were centrifuged at 20,000 g for 10 min and supernatants decanted for P concentration analyses. Phosphates remaining in filtrates or supernatants were analyzed by the methods described above. The amount of phosphate adsorbed was determined by taking the difference between the initial and final concentrations of P in the solutions. The experiment was discontinued at the end of 168 h and the suspensions were centrifuged. A 50 ml aliquot of each supernatant was taken for further analysis and the rest was discarded. The sediment was freeze dried and stored at room temperature for future experiments.

5.2.4. Evaluation of surface charge

To evaluate the surface charge of the clay minerals, back titration (Duquette and Hendershot, 1993) was carried out using a Mettler DL21 titrator. The titration data were collected by computer via an IOtech Serial 488/4 Bus Converter and IOtech MacSCSI 488 Bus Controller. A 0.5 g of clay sample was equilibrated with 80 ml of 0.01 M Ca(NO₃)₂ electrolyte for 24 h. Then the suspension was titrated with 0.05 ml of standardized 0.1 M HNO₃, with 30 s equilibration periods between each addition, until a pH of 3 was reached. The suspension was then divided into two equal portions. One part, as the sample, was weighed and back-titrated automatically with standardized 0.005 M Ca(OH)₂ at a titration rate of 0.05 ml per 10 s to pH 10. The other portion was transferred into a pre-weighed 50 ml centrifuge tube and centrifuged for 5 min at 10,000 g. The clear supernatant, as the reference, was weighed and transferred into a 150 ml beaker. The
reference solution was then back-titrated. The surface charge due to hydroxyl consumption was calculated by subtracting the OH⁻ consumption of the reference from that of the sample.

5.2.5. Released hydroxyl measurement

To keep a relatively constant pH during P adsorption, the pH of the suspension was adjusted to the initial pH after 1, 2, 4, 8, 48, and 72 h of sorption reaction. The pH of a blank suspension, explained above, was also adjusted at the same time. To counter the variation of pH, 0.05M NaOH or HCl was added in the rate of 0.05 ml per 10 s using the automated titrator for both P-containing and blank suspensions. The difference between the amount of NaOH or HCl used for the blank and P-containing suspensions was assumed to be equivalent to the hydroxyl released by P sorption. The pH of suspensions for sepiolite samples increased during the experiment, while for the palygorskite suspension, which was initially adjusted at pH 8, the pH was decreased.

5.2.6. Equations to describe kinetics of P sorption

A number of equations have been used to describe the kinetics of soil chemical processes (e.g., Sparks, 1985, 1986). However, conformity of kinetic data to a particular equation does not necessarily mean that it is the best model, nor can one propose mechanisms based on this alone. The kinetic models examined in this study are presented in Table 5.1. Only one was chosen for describing the kinetics of the adsorption of inorganic and organic phosphates by the clay minerals under various experimental conditions.
Table 5.1. Kinetic models by which organic and inorganic P sorption were examined

<table>
<thead>
<tr>
<th>Model</th>
<th>Linearized equation†</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st-order Kinetics</td>
<td>$\ln [A] = \ln [A]_0 - kt$</td>
<td>Bunnet (1986)</td>
</tr>
<tr>
<td>2nd-order Kinetics</td>
<td>$1/[A] = 1/[A]_0 + kt$</td>
<td>Bunnet (1986)</td>
</tr>
<tr>
<td>Parabolic diffusion equation</td>
<td>$q_t = Kt^{1/2} + B$</td>
<td>Cooke (1966)</td>
</tr>
<tr>
<td>Modified Freundlich</td>
<td>$\ln q_t = \ln (K[A]_0) + 1/m \ln t$</td>
<td>Kuo and Lotse (1974)</td>
</tr>
<tr>
<td>Elovich equation</td>
<td>$q_t = (1/Y) \ln (XY) + (1/Y) \ln (t)$</td>
<td>Chien and Clayton (1980)</td>
</tr>
</tbody>
</table>

†$[A]$ P concentration at time t (M) $q_t$ sorbed P at time t (cmol/kg)
$[A]_0$ initial P concentration (M) $k$ rate constant (h⁻¹)
t time (h) $K$, $B$, $X$, $Y$, and $m$ parameters

5.3. RESULTS AND DISCUSSION

The results of organic and inorganic P adsorption by Sep-Ca at different reaction time and pH are shown in Table 5.2. The adsorption of both IHP and Pi was more rapid initially and leveled off after almost 8 h. More than 85% of adsorption was completed in 8 h reaching to about 95% after 24 h. The change between 1 and 7 d was small, indicating that the 24 h of equilibration used in most of the measurements in this work (Chapter 4) represent a relatively stable condition.

At the beginning of the reaction, the adsorption sites were surrounded by a higher concentration of the adsorbate; the reaction thus went on more easily. As the adsorption proceeded further, less active sorption sites (e.g., hydroxo and or aqua groups) became available for P adsorption (Rajan, 1976) and intraparticle diffusion may have become
Table 5.2. The effect of time on amount and the proportion of organic and inorganic phosphates sorbed by Sep-Ca at different pH

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>IHP</th>
<th></th>
<th></th>
<th></th>
<th>Pi</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH = 6</td>
<td>pH = 7</td>
<td>pH = 8</td>
<td></td>
<td>pH = 6</td>
<td>pH = 7</td>
<td>pH = 8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>q_t</td>
<td>%q_t/Q_T</td>
<td>q_t</td>
<td>%q_t/Q_T</td>
<td>q_t</td>
<td>%q_t/Q_T</td>
<td>q_t</td>
<td>%q_t/Q_T</td>
</tr>
<tr>
<td>0.167</td>
<td>17.28</td>
<td>56.04</td>
<td>15.53</td>
<td>58.97</td>
<td>14.01</td>
<td>63.79</td>
<td>0.534</td>
<td>47.51</td>
</tr>
<tr>
<td>1.000</td>
<td>20.44</td>
<td>66.28</td>
<td>17.60</td>
<td>66.86</td>
<td>15.28</td>
<td>69.54</td>
<td>0.681</td>
<td>60.59</td>
</tr>
<tr>
<td>8.000</td>
<td>28.21</td>
<td>91.48</td>
<td>22.32</td>
<td>84.75</td>
<td>19.03</td>
<td>86.61</td>
<td>0.938</td>
<td>83.45</td>
</tr>
<tr>
<td>24.00</td>
<td>29.68</td>
<td>96.26</td>
<td>24.05</td>
<td>91.33</td>
<td>19.98</td>
<td>90.94</td>
<td>1.030</td>
<td>91.64</td>
</tr>
<tr>
<td>96.00</td>
<td>30.81</td>
<td>99.92</td>
<td>26.32</td>
<td>99.94</td>
<td>21.74</td>
<td>98.94</td>
<td>1.118</td>
<td>99.47</td>
</tr>
<tr>
<td>168.0</td>
<td>30.84</td>
<td>100.0</td>
<td>26.33</td>
<td>100.0</td>
<td>21.97</td>
<td>100.0</td>
<td>1.124</td>
<td>100.0</td>
</tr>
</tbody>
</table>

† q_t: amount of P adsorbed at any time (cmol/kg).
‡ %q_t/Q_T: percentage of sorbed P at any time over that sorbed over one week.
important. The adsorbed phosphate ions could hinder the approach of free phosphate ions from solution to the solid surface by imposing electrical and steric effects (surface potential and space). These factors could explain the difference in the magnitude of P sorption during the different reaction periods. Increase in pH reduced the amount of P adsorbed in all samples; however, the change in the P adsorption was more distinct for sepiolite than for palygorskite.

5.3.1. Choice of kinetic model

The different equations given in Table 5.1 were examined to describe the experimental data. The degree of fit of the data to each model was evaluated based on the $R^2$ (determination coefficient) and the p (probability) values. As an example, the statistical results showing the goodness of different models for adsorption of inorganic P by Pal-Ca at pH 7 are given in Table 5.3. The plots of the equations are presented in Figure 5.1. The kinetic plotting for the adsorption data showed a curvilinear behavior, indicating a multiple kinetic process.

There were two rate process in the reaction period as illustrated in Figure 5.1. The fast reaction occurred between 0.033 - 8.66 h and the slow after 8.66 h. The regression equations were examined for the two reaction periods individually. The $R^2$ values were all significant with a confidence interval of more than 95%, while the parabolic diffusion equation, Freundlich-type, and Elovich equation better described the data than the first and second-order kinetics. In comparison with chemical kinetic equations (i.e., 1st- and 2nd- order), the problem with the use of diffusion, Freundlich-type, and the Elovich equations is that the derived parameters are not well defined physico-chemically (Chien and Clayton, 1980; Sparks, 1986). Therefore, they may not provide a good theoretical basis for the adsorption reaction. However, as empirical equations, they describe the sorption behavior of minerals which is useful for different applications. In this study, the

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Figure 5.1. Multiple kinetic plotting of Pi adsorption by Pal-Ca at pH 7.
<table>
<thead>
<tr>
<th>Model</th>
<th>Regression equation†</th>
<th>Sorption period (h)</th>
<th>n</th>
<th>R²</th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st-order</td>
<td>ln [A] = 1.8312 - 5.46x10⁻³ t</td>
<td>0.033 - 8.66</td>
<td>9</td>
<td>0.78</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>ln [A] = 1.7853 - 1.03x10⁻⁴ t</td>
<td>8.66 - 168.0</td>
<td>6</td>
<td>0.80</td>
<td>0.015</td>
</tr>
<tr>
<td>2nd-order</td>
<td>1/[A] = 0.1602 + 8.45x10⁻⁴ t</td>
<td>0.033 - 8.66</td>
<td>9</td>
<td>0.75</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>1/[A] = 0.1677 + 1.764x10⁻⁵ t</td>
<td>8.66 - 168.0</td>
<td>6</td>
<td>0.69</td>
<td>0.030</td>
</tr>
<tr>
<td>Parabolic diffusion</td>
<td>qt = 0.2298 t (¹/²) + 0.3832</td>
<td>0.033 - 8.66</td>
<td>9</td>
<td>0.95</td>
<td>0.000</td>
</tr>
<tr>
<td>equation</td>
<td>qt = 0.0219 t (¹/²) + 0.9934</td>
<td>8.66 - 168.0</td>
<td>6</td>
<td>0.88</td>
<td>0.005</td>
</tr>
<tr>
<td>Modified</td>
<td>ln qt = -0.4071 + 0.1805 ln t</td>
<td>0.033 - 8.66</td>
<td>9</td>
<td>0.99</td>
<td>0.000</td>
</tr>
<tr>
<td>Freundlich</td>
<td>ln qt = -0.1451 + 0.0749 ln t</td>
<td>8.66 - 168.0</td>
<td>6</td>
<td>0.94</td>
<td>0.001</td>
</tr>
<tr>
<td>Elovich</td>
<td>qt = 0.693 + 0.1118 ln t</td>
<td>0.033 - 8.66</td>
<td>9</td>
<td>0.96</td>
<td>0.000</td>
</tr>
<tr>
<td>equation</td>
<td>qt = 0.826 + 0.0859 ln t</td>
<td>8.66 - 168.0</td>
<td>6</td>
<td>0.95</td>
<td>0.001</td>
</tr>
</tbody>
</table>

† [A] P concentration at time t (Mx10⁻⁴)
  t time (h)
  qt sorbed P (cmol/kg) at time t

kinetics of phosphate adsorption, as a multiple reaction, was described by the modified Freundlich-type equation.
5.3.2. Inorganic P sorption

The inorganic P sorption kinetics of Pal-Ca and Sep-Ca samples at pH 7 are presented in Figure 5.2. Over the fast reaction period the P sorption of Pal-Ca shows a lower initial P sorption with a larger slope than the sepiolite sample. The larger particle size of palygorskite than sepiolite (Chapter 3) may result in lower P sorption at the beginning of the reaction, while higher surface affinity of palygorskite for phosphate ligands, due to its structural Al atoms (Chapter 4), would increase the speed of the P sorption reaction. The slow reaction kinetics revealed that the P sorption for palygorskite continues over a longer period of time, while sepiolite more rapidly reaches its adsorption maximum and the adsorption over the slow reaction period is negligible. This also might be explained by the smaller particle size of sepiolite sample, which results in higher accessibility of sorption sites.

![Figure 5.2. Multiple kinetic plotting of inorganic P sorption by Pal-Ca and Sep-Ca at pH 7.](image)

83
5.3.3. Inositol hexaphosphate sorption.

The IHP sorption kinetics of Pal-Ca and Sep-Ca are presented in Figure 5.3. Organic P sorption capacity of the two mineral is much higher than that of inorganic P. This shows that the mechanism of reaction with the clay surfaces is different for the two types of phosphates. The IHP and Pi ligands seem to be retained by different sorption sites on the clay surfaces. The number of sorption sites for IHP is controlled by the surface area of the clay minerals rather than their structural Al contents. As indicated in Figure 5.3, within 2 min (first sampling), close to 50% of IHP sorption is completed in sepiolite and then the reaction continues for more than 24 h with a relatively slow speed. The sorption reaction levels off after about 24 h. The high initial IHP sorption of sepiolite may be due to the small particle size of this mineral, while as sorption reaction proceeds further, the surface coverage of clay by sorbed ligands, as well as , IHP concentration of
the solution become limiting factors that reduce the speed of the reaction. In the case of palygorskite, the relatively smaller surface area of the mineral provides a lower number of sorption sites initially. The diffusion of sorbed ligands into the aggregates and the higher concentration of IHP in the solution, as compared to that of sepiolite, may then result in a faster sorption reaction up to saturation of the mineral.

5.3.4. Effect of surface cation

The type of surface cation did not influence the speed of P sorption reaction; however, the amount of P sorption was higher when Ca$^{2+}$ was the surface cation. In a study of the effect of surface cation on P sorption of kaolinite and montmorillonite, Bar-Yosef et al. (1988) showed that calcium-clay adsorbed about 10% more P at a given P solution concentration and pH than the K-saturated clay. The kinetics of fast P sorption by Ca- and K- saturated palygorskite is presented in Figure 5.4. The Freundlich-type

![Figure 5.4. Inorganic P sorption kinetics of Pal-Ca and Pal-K at pH 7.](image)
plotting shows almost the same slope for the two samples, while the intercepts were different. This shows that the type of surface cation is not causing any change to the kinetics of P sorption; however, the formation of Ca-phosphate complexes decreases the soluble P. The Ca-phosphates could be formed either on the clay surfaces or as a separate phase. Kinetic plotting of both organic and inorganic P sorption by other samples also showed the same pattern as discussed for palygorskite.

5.3.5. Effect of pH

The kinetics of P sorption was examined at pH values of 6, 7, and 8. The increase in pH decreased the amounts of phosphate sorbed and slowed the sorption reaction in almost all the samples. The general effect of pH on P adsorption reported herein agrees with earlier reports by Muljadi et al. (1966), Murrman and Peech (1969), Bowden et al. (1980), Sanchez and Uehara (1980), Traina et al. (1986), and Ioannou et al. (1994). The role of pH on P sorption may be examined from several different aspects of which the important ones are (i) its effect on the relative fraction of the various P species, which differ in their affinity to the adsorbent; (ii) the variations in the charge density of clay edges with pH; and (iii) the competition between OH⁻ and P for common adsorption sites.

The Freundlich-type kinetic plotting of inorganic P sorption by Pal-Ca over the fast reaction at different pH values is presented in Figure 5.5. As revealed by the Figure, at a given reaction time, phosphate adsorption increases with decreasing pH. This is in agreement with data obtained by Muljadi et al. (1966), Hsu (1968) and Ioannou et al. (1994). It is believed that as a major mechanism, phosphate sorption takes place through exchange of coordinated water molecules at the edge of the clay crystals. Therefore, increasing the number of edge H₂O groups at lower pH favors phosphate adsorption. However, as pH increases, the coordinated water molecules release protons and convert to hydroxyl ligands, which have a higher bonding energy to the clay surfaces, and thereby decrease phosphate adsorption by the ligand exchange mechanism.
Figure 5.5. The inorganic P adsorption kinetics of Pal-Ca at different pH.

The IHP sorption of clay samples also increased at lower pH values. The kinetics of IHP sorption for Sep-Ca and Pal-Ca samples, at different pH values, are shown in Figures 5.6 and 5.7, respectively. The increase in IHP sorption of sepiolite that was induced by the lower values of pH was more pronounced, as compared to that of Pal-Ca sample. The changes in the slope of kinetic lines induced by pH variation, for Pal-Ca and Sep-Ca, are illustrated in Figure 5.8. The Figure shows that the P sorption reaction in sepiolite is more pH dependent than that of palygorskite.

A decrease in pH enhances the speed of P sorption by sepiolite. This may be due to either an increase in the number of aqua sites or a decrease in the negative charge of clay surfaces at lower pH. It has been extensively reported that the deprotonation of coordinated water molecules at clay surfaces, as well as development of surface charges.
Figure 5.6. The IHP sorption kinetic of Sep-Ca at different pH.
due to an increase in pH, have a significant control over P sorption phenomena. Since the development of the surface charge of colloids is controlled by the suspension pH, the pH of adsorption systems would presumably affect the kinetics of the adsorption of phosphate.

\[
\frac{1}{m} = 0.2285 - 0.02165 \text{ pH} \\
R^2 = 0.99
\]

\[
\frac{1}{m} = 0.1695 - 0.00024 \text{ pH} \\
R^2 = 0.99
\]

\[\text{Pal-Ca}\]
\[\text{Sep-Ca}\]

Figure 5.8. Slope of Freundlich-type kinetic, \(1/m\), for IHP sorption against pH.

5.3.6. The pH dependent surface charge of palygorskite and sepiolite

To investigate the different response of palygorskite and sepiolite to pH variation, the surface charge of these minerals was examined at different pH. By back-titration of the sample it is possible to obtain a measure of the \(\text{OH}^-\) interacting with the surface (Duquette and Hendershot, 1993). Figure 5.9 presents a typical back-titration, and the resulting curve for the \(\text{OH}^-\) consumption by the palygorskite and sepiolite surfaces at different pH. The curves for the surfaces are assumed to be due only to the \(\text{OH}^-\)
consumed by the pH-dependent surface functional groups. The surface charge due to hydroxyl consumption was calculated by subtracting the OH⁻ consumption of the reference sample from the sample back-titration at the same pH. According to Duquette and Hendershot (1993), the difference between the amount of OH⁻ consumed by the surface at pH 3 and pH 8, would give a measure of pH-dependent CEC of minerals.

![Graph](image.png)

Figure 5.9. Back titration curve of palygorskite and sepiolite samples.

As indicated in Figure 5.9, the amount of variable surface charge for sepiolite is much higher than that of palygorskite. The larger surface area of sepiolite may explain its higher number of surface functional groups that respond to the pH variation. Also, as reported by Serna et al. (1977) and Serna and Van Scoyoc (1979), due to the higher crystal imperfection, the number of silanols (Si-OH) as surface pH-dependent functional groups in sepiolite is higher than that of palygorskite. Therefore, a change in pH of the system may sharply change the affinity of sepiolite surfaces for P sorption. In contrast, by having a smaller surface area and a lower surface density of silanol groups,
palygorskite shows more stable sorption characteristics over the pH range of the experiment.

5.3.7. Phosphate sorption and release of OH

The release of ligands, especially OH\(^-\) coordinated to the surface sites, is often referred to as the consequence of specific adsorption of phosphate by minerals. Breeuwsma (1973) suggested that, depending on pH, OH\(_2\) molecules are exchanged by phosphate from positive surface groups, and OH\(^-\) ions from uncharged or negative groups. This exchange should result in a ratio of adsorbed phosphate to released OH\(^-\) of between 0 at low pH and 1 at high pH. The increase in P adsorption with decreasing pH was explained by an increasing ratio of OH\(_2^+\) : OH\(^-\) surface groups. The measured OH\(^-\) release rates gives evidence for involvement of a ligand exchange mechanism, but they are often difficult to interpret quantitatively since both phosphate ions and surface sites can accept or release protons (Hingston et al., 1972; Mott, 1981). Thus, the net result of proton adsorption-desorption at the phosphated surface is reflected by the molar ratio of OH\(^-\) released per phosphate adsorbed.

In this study, the net consumption of hydrochloric acid, which was required for maintaining the system pH, was converted into the amount of hydroxyl ions replaced from clay surfaces by adsorbed phosphate ions. The net consumption was calculated based on the difference between the amounts of acid needed for the sample and the blank. The molar ratio (R) of OH\(^-\) released to P adsorbed was then calculated.

The desorption of OH\(^-\) follows almost the same pattern as the P sorption; however, the amount of OH\(^-\) released at the beginning of the sorption reaction is much smaller than that of sorbed P. The relationship between OH\(^-\) released and IHP sorption of Pal-K at pH 8 is illustrated in Figure 5.10. It seems that at the beginning of P sorption by the clay mineral the contribution of hydroxyl exchange to P sorption is relatively low,
but as the reaction proceeds the amount of OH\textsuperscript{-} replaced by sorbed phosphates increases, and after about 20 h it accounts for about 50\% of total P adsorbed.

No release of hydroxyl due to Pi sorption on the palygorskite sample at pH 6 was detected; however, the pH of both the sample and the blank increased slightly during the one week duration of the experiment, which may be due to the hydrolysis of surface cations. This shows that at lower pH, phosphate sorption of palygorskite mostly takes place at aqua sites, whereas at higher pH, ligand exchange with hydroxyl becomes an important mechanism.

The IHP sorption of sepiolite indicated a relatively larger response to variation of pH (Figure 5.6) than that of palygorskite (Figure 5.7). At all the three pH values examined, the P sorption of sepiolite increased the pH of the electrolyte significantly. The titration of released hydroxyls for this sample showed that even at pH 6, the OH\textsuperscript{-} ligand

![Figure 5.10. The OH\textsuperscript{-} released and R against the amount of IHP sorbed by Pal-K at pH 8. R is the cumulative molar ratio of OH\textsuperscript{-} released to P adsorbed.](image-url)
exchange contributes up to about 25% of phosphate sorption. The cumulative molar ratio of desorbed OH\textsuperscript{-} to sorbed P increases with pH and reaches about 60% at pH 8, similar to that for palygorskite (Figure 5.10). The higher R values for sepiolite over the range of pH examined, may indicate the different surface chemistry of the two minerals. Sepiolite possesses a higher number of surface OH\textsuperscript{-} sites than palygorskite. This is in agreement with the results of the back titration experiment (Figure 5.9).

The lower R values at the beginning of P sorption reaction reveal that coordinated water molecules at the clay surfaces preferentially react with the phosphate ligands. As the degree of surface coverage by sorbed phosphate increases, the number of remaining surface-water molecules becomes a limiting factor, increasing the contribution of surface hydroxyl sites to P sorption. It may be concluded that during the fast P sorption reaction, the exchange of coordinated water molecules is the main mechanism controlling the P sorption, followed by OH\textsuperscript{-} ligand exchange in the slow sorption reaction. This is in agreement with the findings of Rajan (1975). He concluded that at low surface coverage of the phosphate adsorption sites, the exchange mainly occurred at aqua sites releasing H\textsubscript{2}O molecules, but at high surface coverage the hydroxyl groups became the predominant active sites in the adsorption of P and were concomitantly released by a ligand exchange reaction.

5.4. CONCLUSIONS

Phosphate sorption on soil components is a time dependent reaction. In this study, the kinetics of orthophosphate (Pi) and inositol hexaphosphate (IHP) sorption on palygorskite and sepiolite were investigated, with a focus on kinetic modeling and the effects of surface cations and the pH of the electrolyte on sorption reactions. The clay samples used were palygorskite and sepiolite saturated with Ca\textsuperscript{2+} and K\textsuperscript{+} (Pal-Ca, Pal-K, Sep-Ca, and Sep-K), and the pH of sorption reactions was established at 6, 7, and 8.
The results of P sorption experiments showed that for both minerals and at different pH, adsorption of Pi and IHP was more rapid initially and then leveled off after about 8 h. At the beginning of the reaction, due to the higher concentration of available sorption sites and the adsorbate, the reaction proceeds more easily; however, with time, the active sorption sites and the solution concentration diminish and a slow diffusion becomes more important.

Over the fast reaction period the Pi sorption of Pal-Ca showed a lower intercept with a larger slope than the sepiolite sample. The larger particle size of palygorskite over that of sepiolite may result in a lower amount of P sorption at the beginning of the reaction, while its higher affinity for phosphate ligands would increase the speed of the P sorption reaction. The slow reaction kinetics revealed that the P sorption for palygorskite continues over a longer period of time than sepiolite; sepiolite more rapidly reaches its adsorption maxima and the adsorption over the slow reaction period is negligible. This also might be explained by the smaller particle size of the sepiolite sample which results in higher accessibility of sorption sites.

The type of surface cation apparently did not affect the speed of the sorption reaction; however, Ca$^{2+}$ induced a higher initial P sorption than K$^+$. Formation of Ca-phosphate complexes on clay surfaces may be a mechanism causing the higher sorption capacity of Ca-saturated minerals. The pH of the system decreased the slope of both inorganic and organic phosphate sorption kinetics; this effect was more pronounced in sepiolite. To investigate the different response of the minerals to pH variation, the surface charge of the minerals was examined at different pH levels by back titration. The results showed that sepiolite possesses a higher number of pH-dependent surface functional groups than palygorskite. This may result in a larger increase of negative charges in sepiolite due to the increase of pH when compared with that of palygorskite. Therefore, the P sorption characteristics of sepiolite may be more pH dependent than those of palygorskite.
The specific sorption of phosphates on the clay minerals was investigated by measurement of released hydroxyls. Release of $\text{OH}^-$ due to Pi sorption of palygorskite at pH 6 was not detectable, suggesting that at lower pH aqua sites are more important, and that as pH increases, ligand exchange with hydroxyl becomes more significant. The ratio of hydroxyls released to sorbed phosphate also showed that at the beginning of P sorption reactions, even at higher pH values, the contribution of hydroxyl exchange to P sorption is relatively low, but as the reaction proceeds the amount of $\text{OH}^-$ replaced by sorbed phosphates increases; in IHP sorption by Pal-K at pH 8, after about 20 h it accounted for about 50% of total P adsorbed.
CHAPTER 6
AVAILABILITY OF SORBED PHOSPHATE BY
PALLYGORSKITE, SEPIOLITE, AND MONTMORILLONITE
IN A CARBONATIC SYSTEM

6.1. INTRODUCTION

Carbonates exist with palygorskite and sepiolite in most soils of arid and semiarid regions. Electron microscope studies showed that larger calcite crystals are usually covered by the relatively small and tiny palygorskite and/or sepiolite fibers (Singer, 1989; Botha and Hughes, 1992; Khademi, 1997). This association suggests that these fibrous clay minerals provide a large reactive surface area, even in the presence of carbonates, which may significantly influence the sorption behavior of the soil in which they occur.

Studies of phosphate interactions with relatively pure minerals revealed that the P sorption capacity of palygorskite and sepiolite is higher than that of other crystalline silicate clay minerals (Chapter 4). The P sorbed by these silicate clay minerals seemed to be easily released to the soil solution. However, quantitative information on the availability of sorbed phosphates by these minerals in a natural system is still lacking. In this work, the availability of P sorbed by these fibrous silicate clay minerals, in the presence of calcite, was investigated similar to the natural conditions. A montmorillonite that can co-exist with palygorskite and sepiolite in soils, was also included in the experiment. The objectives of this part of the work were to:

1. study the desorption of sorbed P by palygorskite and sepiolite using different organic ligands,
2. compare the availability of sorbed P on palygorskite and sepiolite with that of montmorillonite in pure clay and in clay-calcite combinations,

3. determine the factors controlling P availability in the clay-calcite system,

4. evaluate and compare the ability of some simple empirical equations to describe P desorption Q/I relationships.

6.2. MATERIALS AND METHODS

6.2.1. Phosphate compounds

Sodium salts of orthophosphate (Pi) (Fisher, ACS) and inositol hexaphosphate (IHP) (BDH) were used in this study. The phosphorus contents of all phosphates studied were determined experimentally, as explained in Chapter 4. The EC and pH of the P solutions were adjusted at 2 dS m\(^{-1}\) and 7.0, respectively, using 1 M KCl and either 0.05 N NaOH or HCl. Chloroform was added in the ratio of 1 ml to 1 L of the solution to prohibit microbial activities.

6.2.2. Clay-calcite combinations

Three silicate clay minerals and one calcite sample were used in this experiment. The clay minerals were: 1. palygorskite PFI-1 and 2. montmorillonite STx-1, both from Clay Mineral Society repository source (CMS), and 3. sepiolite, a geological sample obtained from Eskishehir, Turkey. To remove the phosphate impurities, the palygorskite sample was treated with Na-OAc buffered at pH 4 as explained in Chapter 3. The montmorillonite and sepiolite samples were treated with Na-OAc of pH 5 (Jackson, 1979) to remove carbonatic impurities. The purified clays were then homoionized with either 1 N CaCl\(_2\) or KCl followed by freeze-drying. The homoionized clay samples used for this study were: sepiolite Ca\(^{2+}\)-saturated (Sep-Ca), sepiolite K\(^{+}\)-saturated (Sep-K),
palygorskite Ca$^{2+}$-saturated (Pal-Ca), palygorskite K$^+$-saturated (Pal-K), and montmorillonite Ca$^{2+}$-saturated (Mont-Ca).

Calcite (CaCO$_3$) was included because it is the prevailing mineral in palygorskitic soils. The calcite used in this work was a Fisher laboratory sample (Lot # 793932) with a BET surface area measured as 0.8 ±0.1 m$^2$ g$^{-1}$. To quantify the P sorption/desorption of palygorskite and sepiolite in a carbonatic system, different mixtures of clay-calcite were examined. The mixtures were; pure calcite, 10% calcite + 90% clay, 5% calcite + 95% clay, and pure clay. To compare the P desorption of palygorskite and sepiolite with that of other silicate clays dominant in arid soils, combinations of montmorillonite-calcite were also included in the experiment.

6.2.3. Mineral suspension

A 3.75 g mineral mixture was suspended in about 80 ml deionized water in a 200 ml volumetric flask at room temperature for 48 h. For dispersion of aggregates and hydration of adsorption sites, the suspension was stirred for 30 min periods, with 5.5 h rest intervals, using a magnetic stirrer. The pH of suspensions was adjusted to 7.0 at 12, 24, and 48 h after soaking, using a Mettler DL21 automated titrator. The initial pH of suspensions containing sepiolite and calcite were above 7.0, and minor amounts of 0.05 M HCl were applied to bring the pH to 7.0. In pure Pal-Ca and Mont-Ca suspensions, the pH was almost 7.0 and no acid addition was needed. Before the P sorption experiment the volume of suspension was increased to 150 ml while its EC and pH were adjusted at 2 dS m$^{-1}$ and 7.0, respectively, using 0.1 M KCl and 0.05 M HCl or NaOH solution. The EC of solutions was measured using a CDM 83 electrical conductivity meter equipped with a CDC 114 pipette cell. To suppress the microbial activity in the clay suspensions, chloroform was added in the ratio of 1 ml to 1 L of the suspension.
6.2.4. Adsorption for desorption experiment

Adsorption of phosphate was achieved by adding 15 ml of a solution with a P concentration of 2.2 mM for Pi and 7.5 mM for IHP, adjusted at pH 7.0 and EC of 2 dS m\(^{-1}\) to 10 ml of a suspension containing 0.25 g clay or mineral mixture adjusted at the same pH and EC. The mixture was shaken for 24 h at a constant temperature (24 ±1°C) in pre-weighted 50 ml polyethylene centrifuge tubes. The clay-to-solution ratio was 1/100. Phosphate sorption saturation of the clay minerals was adjusted to about 100% of maximum sorption, according to the previously established sorption isotherms (Chapter 4). Next, the suspension was centrifuged for 15 min at 20,000 g to obtain a clear solution for P measurements.

6.2.5. Interactions of clay-calcite mixtures

To study the clay-calcite interactions that affect the P sorption/desorption behavior, some physico-chemical properties of the mixtures were investigated. Mixtures were studied visually under a Scanning Electron Microscope (SEM). The specimens were prepared by drying some drops of the suspensions on the sample stubs. The dried samples were then examined by a Philips model 505 SEM. Surface area of freeze dried samples was measured by the BET method with nitrogen gas as an adsorbate (Brunauer et al., 1938), using an Autosorb-1 Quantachrome instrument.

The chemistry of equilibrium P sorption solution for different samples was also studied by elemental analyses of the electrolytes. In addition to P concentration measurements, the total soluble Si was determined by colorimetry (Black et al., 1965), Al, Ca, and Mg by atomic absorption, and K and Na by atomic emission spectrophotometry using a Perkin Elmer 3100 Atomic Absorption Spectrometer.
6.2.6. Desorption of phosphates

The reversibility of sorbed P was examined using different organic ligands as P extractants. In this work a sequential extraction was carried out to perturb the equilibrium in the experimental solutions. All treatments were performed in two replicates. To assess the reversibility of sorbed P, the total P desorbed, Q, is plotted against the equilibrium P concentration, I, in the solution and the ability of three empirical models to describe the desorption data was examined.

6.2.6.1. Organic acids/anions

Citric, oxalic, succinic, and aspartic acids were selected for the study, because they occur naturally in significant quantities in soils (Stevenson, 1967; Hue et al., 1988; Hue, 1991) and they differ in number and type of functional groups. Citric acid has one hydroxyl and three carboxyl groups. Aspartic acid has two carboxyl and one amine groups which may interact with negatively charged surface sites. Oxalic and succinic are dicarboxylic acids, but differ in carbon chain lengths and molecular weights. Consequently, the reactivity of these acids with soil minerals is expected to be different. Table 6.1 lists the chemical structure and dissociation constants of these acids.

A concentration of 2x10^{-3} M of the organic acids was prepared in KCl while the final pH and EC of electrolyte were adjusted at 7.0 and 2 dS m^{-1}, respectively. One aliquot of KCl electrolyte with the pH of 7.0 and EC of 2 dS m^{-1} was prepared with no addition of organic acid as the control. The pH of the solutions was adjusted to 7.0 with NaOH. The pH 7.0 was selected in an attempt to simulate the natural pH of the palygorskitic environments. Chloroform was added in the ratio of 1 ml per 1 L of electrolyte to suppress the microbial activity, and the electrolytes were stored in 2 L amber jars and kept in a dark place during the experiment to prevent the decomposition of the acids in light. Because the pK_{1} of all acids was below pH 7.0, all acids are dissociated
and their conjugated anions were present in the KCl solutions at this pH. For simplicity, however, the term "organic acid" will be used hereafter to address the conjugate anions.

Table 6.1. Chemical structure and dissociation constants of the organic acids used in the desorption experiments (Weast and Astle, 1980)

<table>
<thead>
<tr>
<th>Organic acid</th>
<th>Chemical structure</th>
<th>MW†</th>
<th>Dissociation constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>pK₁</td>
</tr>
<tr>
<td>Citric</td>
<td>COOH-CH₂-C-C-COONH</td>
<td>192</td>
<td>3.14</td>
</tr>
<tr>
<td>Oxalic</td>
<td>HOOC - COOH</td>
<td>90</td>
<td>1.23</td>
</tr>
<tr>
<td>Succinic</td>
<td>COOH - CH₂ - CH₂ - COOH</td>
<td>118</td>
<td>4.16</td>
</tr>
<tr>
<td>Aspartic</td>
<td>NH₂ - CH - CH₂ - CH₂ - COOH</td>
<td>147</td>
<td>1.88</td>
</tr>
</tbody>
</table>

†MW = molecular weight (g)

6.2.6.2. Sequential extraction

For the P desorption studies, 25 ml of the different P extractants were added to the tubes containing 0.25 g of clay or mineral mixtures preloaded with phosphate in the P adsorption step. The tubes were capped, shaken vigorously by hand, followed by multivortexing to bring the clay samples into suspension, and then placed in a rotary shaker and shaken at room temperature (24 ± 1°C). The time period used for each desorption sequence was 24 h and seven subsequent desorptions were carried out. At the end of each time period, the samples were centrifuged for 15 min at 20,000 g and the clear supernatant was removed for P measurement. Then the tubes with the sample
residue were weighed, 25 ml of electrolyte were added, and the samples were vortexed
and then placed on the rotary shaker.

The tubes containing the samples were weighed after each desorption to determine
the solution P carried over to the next desorption. This amount was then subtracted from
the P desorbed in the next extraction. The P concentrations in successive volumes were
measured and the total P desorbed from the soil was calculated by summing successive
removals (Brewster et al., 1975). The amount of phosphate desorbed from the samples
was corrected for that from the control sample that received no phosphate treatment.

6.2.6.3. Mathematical models for phosphorus desorption Q/I
relationships

A Q/I curve, as described in Chapter 2, was obtained by plotting total P desorbed
from the mineral (Q) against solution P concentrations (I). The successive solution P
concentrations decreased as more P was exhausted from the minerals. The higher the
amount of cumulative desorbed P or the smaller the solution P concentration, the greater
is the slope of the curve. When P desorption from the sample begins, the solution P
concentration tends to be the highest. When P in the sample is exhausted, the solution P
approaches zero value. The intercept of the Q/I curve on the Q axis is expected to occur
somewhere well above the maximum P extracted after 7 days. Therefore, the Q/I curve
has to be considered asymptotic with respect to the Q axis within the relatively low range
of extractable P.

Three empirical equations were tested for their ability to describe the desorption
Q/I data. These mathematical models were fitted using nonlinear regression procedures
(SAS Institute, 1985). The applied equations were:

- Brewster et al. (1975) \( Q = a + b \ln(I) \)
- Barrow (1979) \( Q = a + b I^c \)
- and Raven and Hossner (1993) \( Q = a I^{-0.1} + b \ln(I + 1) + c \)
where $Q$ is the cumulative desorbed $P$, $I$ is the equilibrium solution $P$ concentration, and $a$, $b$, and $c$ are fitting constants.

6.3. RESULTS AND DISCUSSION

6.3.1. Availability of organic $P$ sorbed by the clay-calcite mixtures

The results of IHP sorption of different minerals examined in this study are shown in Table 6.2. The $Ca^{2+}$-saturated clays showed a relatively higher $P$ sorption capacity than $K^+$-saturated clays. Calcium, as a divalent surface cation, increases the $P$ sorption capacity of the mineral. As explained in Chapter 4, this might be due to the limited extent of the diffuse double layer on clay surfaces-saturated with $Ca^{2+}$. The lower solubility of Ca-IHP complexes may also explain the higher affinity of $Ca^{2+}$-saturated surfaces. Precipitation of Ca-IHP as a separate phase is another possibility for decreasing the phosphate in solution.

Montmorillonite showed a higher IHP sorption capacity than palygorskite. The higher concentration of exchangeable $Ca^{2+}$, in montmorillonite may result in the greater affinity of this mineral for IHP sorption. Sepiolite samples-saturated with Ca showed the highest IHP sorption capacity among the three clay minerals. The larger external surface area of this mineral, compared to those of palygorskite and montmorillonite, is likely to be the main reason of this phenomenon.

The presence of calcite in the mixtures sharply increased the amount of sorbed $P$. As shown in Table 6.2, the amount of sorbed organic $P$ in the presence of even 5% calcite was as much as that of pure calcite. Therefore, one may conclude that in a silicate clay-calcite combination the sorption of organic $P$ is mainly controlled by mineral calcite. The presence of calcite in the mixture may provide a relatively high concentration of $Ca^{2+}$ ions in the solution causing the formation of Ca-IHP complexes. However, the amount of $P$
available in the solution as a limiting factor induced the same levels of P sorbed by
different clay-calcite combinations.

Table 6.2. IHP sorption of different mineral combinations.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>% CaCO₃ of mixtures</th>
<th>Sorbed P (cmol/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palygorskite</td>
<td>Pal-K 0.0</td>
<td>11.5</td>
</tr>
<tr>
<td></td>
<td>Pal-Ca 5.0, 10.0</td>
<td>44.6</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>Mont-Ca 0.0, 5.0, 10.0</td>
<td>21.2, 44.6</td>
</tr>
<tr>
<td>Sepiolite</td>
<td>Sep-K 0.0</td>
<td>21.4</td>
</tr>
<tr>
<td></td>
<td>Sep-Ca 0.0</td>
<td>24.2</td>
</tr>
<tr>
<td>Calcite</td>
<td>100</td>
<td>44.6</td>
</tr>
</tbody>
</table>

6.3.1.1. Organic P desorption isotherms

To describe the equilibrium of IHP with minerals, three multicomponent, electrostatic models were applied (Brewster et al., 1975; Barrow, 1979; Raven and Hossner, 1993). Only the model by Raven and Hossner (1993) has been used to describe the desorption isotherms:

\[ Q = a I^{-0.1} + b \ln(I + 1) + c \]
In the Raven and Hossner equation, increasing the value of \( a \) shifts the Q/I curves upward. The magnitude of the shift is higher at relatively low I values and decreases as I increases. Thus, the higher value of parameter \( a \), the higher the Q values throughout the whole I range, the higher the magnitude of the buffering power at a given relatively low I value, and the greater the change in buffering power in a given I range. The more negative the value of \( b \), the more markedly the Q/I curve bends downward. Making \( b \) more negative reduces the Q, increases the magnitude of the buffering power at relatively high I values. An increase in parameter \( c \) shifts the Q/I curve vertically. The shift is the same throughout the whole I range. This evaluation indicates that the magnitude of the buffering power is predominantly determined by parameter \( a \) at relatively low I values, and by parameter \( b \) at higher I values.

Plots of the Raven and Hossner equation for the IHP desorption data of Pal-Ca in different extractants are shown in Fig. 6.1. The desorption Q/I equation closely described

![Figure 6.1. Plots of the Raven and Hossner equation for IHP desorption isotherms of Pal-Ca in different extractants](image)
the experimental data, as judged from the determination coefficient ($R^2$) values and the mean sum square of residuals (MSR). Tables 6.3 and 6.4 show the values of $R^2$, MSR, and the fitting parameters for the IHP desorption isotherms of Pal-Ca in different organic acids, and those of Clay-CaCO$_3$ in succinic acid. Since $R^2$ alone is not a valid criterion to compare the fitting ability of different equations, MSR was also calculated as a direct indication of the deviation of estimated values from actual data.

The MSR ranged between 0.002 to 0.052 for the Raven and Hossner equation, while it ranged between 0.002 and 0.052, and 0.004 and 0.089 for the Barrow (1979) and Brewster et al. (1975) equations, respectively. Almost for the whole IHP desorption data set, the deviation of estimated values by the Raven and Hossner equation from the actual values was smaller than those of the equations by Barrow and Brewster et al.

Citric acid extracted the most IHP, followed by oxalic acid and succinic acid which were as effective as KCl electrolyte. Possessing three carboxyl and one hydroxyl groups, citrate is a powerful ligand to replace the sorbed phosphates on the clay surfaces. Oxalic and succinic are both dicarboxylic acids that show relatively the same desorption ability in Pal-Ca, although, due to the smaller molecular size, the oxalate ligand seems to be more reactive. The effect of oxalic and succinic acids was almost the same as that of KCl electrolyte. To avoid confusion, the desorption curve for succinic acid is not shown in the Figure 6.1.

The IHP desorption isotherm of Pal-Ca in aspartic acid is located considerably below that of KCl electrolyte. Possessing an amine group, aspartic acid might be adsorbed by the clay surfaces which neutralizes the negative charges and speeds the approach of negative phosphate ligands to the clay surfaces. This is in agreement with the increasing effect of amino acids on P retention of montmorillonite and kaolinite reported by Kafkafi et al. (1988). Regarding the effect of organic acids, the IHP desorption isotherms of other samples were relatively the same as those of Pal-Ca. Figure 6.2 shows the IHP desorption isotherms of Pal-K using different extractants. The maximum
phosphate desorbed was highest for citric acid followed by oxalic acid, succinic acid, KCl, and aspartic acid.

Figure 6.2. The IHP desorption isotherms of Pal-K in different extractants.

The IHP desorption isotherms of Pal- and Mont-CaCO₃ in aspartic acid are illustrated in Figure 6.3. Showing almost the same trends, the IHP desorption isotherms of the clay-calcite combinations in succinic acid are presented in Figure 6.4. The presence of palygorskite in the combination enhances the availability of sorbed IHP over the pure calcite and Mont-CaCO₃ combination. The relatively high external surface area and dispersability of palygorskite may suppress the P fixing characteristics of calcite in the combination. The montmorillonite clay did not increase the availability of sorbed P over the pure calcite mineral.
Table 6.3. The fitting values, MSR, and $R^2$ for different equations describing the IHP desorption of Pal-Ca in different extractants

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<tr>
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<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
<td>c</td>
</tr>
<tr>
<td>KCl</td>
<td>7.646</td>
<td>-6.140</td>
<td>0.049</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>0.327</td>
<td>1.440</td>
<td>-0.491</td>
</tr>
<tr>
<td>Succinic acid</td>
<td>41.29</td>
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</tr>
<tr>
<td>Citric acid</td>
<td>-0.58</td>
<td>7.48</td>
<td>-0.340</td>
</tr>
<tr>
<td>Aspartic acid</td>
<td>4.987</td>
<td>-4.070</td>
<td>0.0537</td>
</tr>
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</table>

Table 6.4. The fitting values, MSR, and $R^2$ for different equations describing the IHP desorption of Clay-CaCO$_3$ in 0.002 M succinic acid

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<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
<td>c</td>
</tr>
<tr>
<td>Pal-CaCO$_3$</td>
<td>1.053</td>
<td>-0.982</td>
<td>0.047</td>
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<tr>
<td>Mont-CaCO$_3$</td>
<td>0.411</td>
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</tr>
<tr>
<td>CaCO$_3$</td>
<td>0.224</td>
<td>-0.1631</td>
<td>0.3159</td>
</tr>
</tbody>
</table>
Table 6.5. The fitting values, MSR, and R^2 for different equations describing the Pi desorption isotherms of different minerals using citric acid.

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<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
<td>c</td>
</tr>
<tr>
<td>Pal-K</td>
<td>1.556</td>
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<tr>
<td>Pal-Ca</td>
<td>2.446</td>
<td>-2.546</td>
<td>0.149</td>
</tr>
<tr>
<td>Pal-CaCO_3 5%</td>
<td>27.370</td>
<td>-24.36</td>
<td>0.019</td>
</tr>
<tr>
<td>Pal-CaCO_3 10%</td>
<td>11.836</td>
<td>-8.330</td>
<td>0.206</td>
</tr>
<tr>
<td>Mont-Ca</td>
<td>4.009</td>
<td>-3.314</td>
<td>0.012</td>
</tr>
<tr>
<td>Mon-CaCO_3 5%</td>
<td>49.830</td>
<td>-47.24</td>
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<tr>
<td>Mon-CaCO_3 10%</td>
<td>0.045</td>
<td>2.832</td>
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<td>Sep-CaCO_3 5%</td>
<td>4.162</td>
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<tr>
<td>Sep-CaCO_3 10%</td>
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<td>CaCO_3</td>
<td>-9.051</td>
<td>11.801</td>
<td>-0.216</td>
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Table 6.6. The fitting values, MSR, and R^2 for different equations describing the Pi desorption isotherms of different minerals using KCl.

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<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
<td>c</td>
</tr>
<tr>
<td>Pal-K</td>
<td>15.058</td>
<td>-14.336</td>
<td>0.021</td>
</tr>
<tr>
<td>Pal-Ca</td>
<td>-7.563</td>
<td>8.879</td>
<td>-0.058</td>
</tr>
<tr>
<td>Pal-CaCO_3 5%</td>
<td>0.37</td>
<td>87709</td>
<td>1334036</td>
</tr>
<tr>
<td>Pal-CaCO_3 10%</td>
<td>0.305</td>
<td>513465</td>
<td>5061483</td>
</tr>
<tr>
<td>Mont-Ca</td>
<td>2.696</td>
<td>-2.225</td>
<td>0.0648</td>
</tr>
<tr>
<td>Mon-CaCO_3 5%</td>
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<td>2044447</td>
</tr>
<tr>
<td>Mon-CaCO_3 10%</td>
<td>0.311</td>
<td>90.596</td>
<td>49.19</td>
</tr>
<tr>
<td>Sep-CaCO_3 5%</td>
<td>16.56</td>
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<td>0.085</td>
</tr>
<tr>
<td>Sep-CaCO_3 10%</td>
<td>-2.192</td>
<td>6.19</td>
<td>-0.40</td>
</tr>
<tr>
<td>CaCO_3</td>
<td>20.227</td>
<td>-20.414</td>
<td>0.018</td>
</tr>
</tbody>
</table>
Figure 6.3. The IHP desorption isotherms of Pal- and Mont-CaCO₃ 10% combinations and pure calcite in aspartic acid.

Figure 6.4. The IHP desorption isotherms of Pal- and Mont-CaCO₃ 10% combinations and pure calcite in succinic acid.
6.3.1.2. The inositol hexaphosphate desorption of pure clays

The IHP desorption isotherms of pure clay minerals in oxalic acid are illustrated in Figure 6.5. The sepiolite sample showed the highest P desorbability, followed by the palygorskite and montmorillonite samples. This order of IHP desorbability was also found using succinic and aspartic acids, but in the case of citric acid and KCl the difference between montmorillonite and palygorskite was not as clear as in Figure 6.5, and montmorillonite showed a relatively higher desorbability than palygorskite. This might be explained by the extraction power of the ligands applied. Being a relatively powerful ligand, citrate replaces the sorbed phosphate on the surface of different clay minerals easily, extracting a relatively high quantity of sorbed phosphate in all clay samples.

![Graph showing desorption of Sep-Ca, Pal-Ca, and Mont-Ca in oxalic acid.](image)

Figure 6.5. The IHP desorption of Sep-Ca, Pal-Ca, and Mont-Ca in oxalic acid.

On the other hand, the Cl⁻ ligand is too weak to replace large phosphate ligands on the clay surfaces, extracting relatively low amounts of phosphate in all clay samples. Using dicarboxylic acids, such as oxalic and succinic as extractants, the stability of the
The ligand-clay complex seems to be compatible with that of phosphate-clay; therefore, any difference in the clay reactivity would affect the amount of phosphate released by these ligands. The difference in the availability of sorbed phosphate by the examined clay minerals is due to their different physical and chemical properties.

The relatively large external surface area of sepiolite induces a high desorbability of sorbed phosphate in a P depleted solution. The replacement of Mg for Al atoms in the sepiolite structure reduces the strength of the phosphate-clay bond; therefore, the sorbed phosphate by sepiolite is more labile than that of the other two clay minerals. The presence of Al atoms in the octahedral sheets of montmorillonite increases phosphate retention by this mineral.

Palygorskite, with its intermediate position in terms of structural aluminum content and external surface area, shows lower desorbability of phosphate than sepiolite, but is much higher than that of montmorillonite. A comparison of IHP desorption isotherms of the clay minerals and calcite is illustrated in Figure 6.6. With a lower total

![Graph](image)

Figure 6.6. The IHP desorption isotherms of Sep-Ca, Pal-Ca, Mont-Ca, and CaCO₃ in succinic acid.
desorbed P, the IHP desorption isotherms of the different minerals in succinic acid have almost the same pattern as those in oxalic acid (Fig 6.5). The desorbability of phosphate sorbed by CaCO$_3$ was lower than that of palygorskite and sepiolite clay minerals. This shows that the solubility of Ca-IHP, which forms either as a surface complex or a separate solid phase, was relatively low under the experimental conditions. Therefore, the higher concentration of surface Ca$^{2+}$ in montmorillonite, which increases the formation of Ca-IHP complexes, might be another reason for the lower desorbability of sorbed organic phosphate by this mineral.

### 6.3.2. Availability of inorganic P sorbed by the clays and clay-calcite combinations

The results of inorganic P sorption of different mineral combinations are illustrated in Figure 6.7. The pure calcite showed the highest P sorption capacity among the different minerals. The presence of 5% to 10% calcite in the palygorskite and montmorillonite-calcite mixtures induces a P sorption capacity as high as that of pure calcite. The sepiolite-calcite showed about 50% reduction in P sorption capacity in comparison with that of calcite, while the P sorption capacity of this combination was far greater than that of pure sepiolite. For the pure clay minerals, the palygorskite sample showed the highest P sorption capacity of 1.5 cmol kg$^{-1}$, followed by sepiolite and montmorillonite with 0.83 and 0.78 cmol kg$^{-1}$, respectively. The large surface area, high dispersability, and possession of structural Al atoms are the main reasons given previously for the higher Pi sorption capacity of palygorskite compared to the other two crystalline silicate clays.

The results indicate that calcite controls the amount of P sorbed in all the clay-calcite combinations; however, sepiolite sharply reduces the P sorption capacity of calcite.
The amount of sorbed P by sepiolite-calcite averaged less than 50% of that by the other combinations. As explained previously, formation of Ca-phosphates may be the main mechanism that removes phosphate ions from the solution in Pal- and Mont-CaCO₃ combinations. However, the presence of sepiolite in the mixture seems, to some degree, to hamper this mechanism.

![Graph showing sorption of P](image)

Figure 6.7. The inorganic P sorption of clay-calcite mixtures.

6.3.2.1. Organic ligands and Pi desorption

The goodness criteria, MSR and R², and the fitting parameters of the three equations that describe the desorption isotherms of minerals examined, using citric acid and KCl, are presented in Tables 6.5 and 6.6. The relationship between curve-fitting parameters and the P enrichment in the sample did not show any specific trend across all.
samples. This result was apparently due to mutual compensation effects of the constants during curve fitting. Therefore, the values of individual parameters are sample-specific and are not able to give any information about the P releasing capacity of the samples.

The Pi desorption isotherms of Pal-Ca in different organic acids are presented in Figure 6.8. The citric acid solution extracted the most Pi, followed by oxalic acid; aspartic and succinic acids and KCl showed the least P desorption.

![Graph showing desorption isotherms](image)

Figure 6.8. Inorganic P desorption isotherms of Pal-Ca in different extractants.

6.3.2.2. Calcite proportion and Pi desorption

Although, the Pi sorption of clay-calcite combinations seems to be controlled by calcite, the presence of clay influences the Pi desorption of the combination. Clay-calcite combinations show a higher Pi availability over the pure calcite in citric acid; however, a higher proportion of calcite would result in lower availability of sorbed Pi.

The inorganic P desorption isotherms of Pal-CaCO3 in citric acid are presented in Figure 6.9. The phosphate released from Pal-CaCO3 containing 10% calcite is higher than
that of pure calcite, especially when the solution P concentration, I, is relatively high. The highest total desorbed P was associated with the combination that possessed the lowest proportion of calcite. The presence of calcite may induce the formation of Ca-phosphate compounds with low solubility that decrease the availability of P in different extractants, while the presence of clays seems to work against this reaction. A possible mechanism is the presence of silicate clay minerals in the combination which may hamper the formation of Ca-phosphate compounds.

Different CaCO₃ proportions in the mixtures showed similar desorption isotherms when using KCl electrolyte as the P extractant. This might be explained by the low P extraction power of KCl, which desorbs insignificant quantities of sorbed P from either CaCO₃ or from Clay-CaCO₃ combinations.

![Graph showing desorption isotherms](image)

Figure 6.9. Inorganic P desorption isotherms of Pal-CaCO₃ combinations in citric acid extractant.
6.3.2.3. Availability of inorganic P sorbed by clay-calcite mixtures

In all the different extractants, Pal-CaCO₃ combinations showed a higher P availability over Mont-CaCO₃ combinations. The inorganic P desorption isotherms of calcite, Pal-, and Mont-CaCO₃ 10% in citric acid are presented in Figure 6.10. The clay-calcite combinations provide higher P concentrations in the solution over pure calcite, while the P sorbed by calcite became available when the P concentration in the solution was relatively low.

![Figure 6.10](image)

Figure 6.10. Inorganic P desorption isotherms of calcite, Pal-, and Mont-CaCO₃ 10% in citric acid.

Regardless of the extractant ligand, the availability of sorbed phosphate by Sep-CaCO₃ far exceeded that of other combinations, and pure calcite. Almost 100% of sorbed phosphate by Sep-CaCO₃ was recovered within seven extractions using citric acid.
The quantities of desorbed phosphate in oxalic acid from different combinations in seven extraction sequences, d1 to d7, are illustrated in Figure 6.11. Over 60% of sorbed phosphate by Sep-CaCO3 was released during the first extraction, followed by about 15% desorption in the second, and less than 5% in the third extraction. The daily P desorption after the 3rd extraction was negligible, the cumulative desorbed phosphate after the 7th extraction accounted for about 90% of the total P sorbed by the sample. The total P desorbed from Pal-CaCO3 was smaller than that of Sep-CaCO3; however, the former kept a relatively constant P concentration in the solution during the period of P extraction. This suggests that the Pal-CaCO3 loaded with P is able to supply P slowly, but over a long period, which is an advantage in the P management in palygorskitic soils. The availability of sorbed P by Mont-CaCO3 was lower than that of Pal-CaCO3. However, it exceeded the availability of CaCO3 sorbed P by a factor of 4. Less than 5% of the total P sorbed by CaCO3 was recovered within seven extraction sequences.

![Graph showing desorption and retention of phosphate](image)

Figure 6.11. The sequential recovery of sorbed Pi (d1 to d7 represent the desorbed P by extraction 1 to 7) from calcite and clay-CaCO3 10% combinations using oxalic acid.
6.3.3. Examination of clay-calcite systems and P sorption/desorption

To investigate the interactions that cause the differences in the availability of sorbed P by the CaCO₃-clay mixtures, some samples were examined by electron microscopy, surface area measurement, and chemical analyses.

Micrographs of different clay-calcite samples are presented in Figures 6.12.a to e. Rhombohedral crystals of pure calcite are illustrated in Figure 6.12.a. Figure 6.12.b shows the original sepiolite sample containing carbonate impurities. The fibrous crystals of sepiolite appear to envelop the particles of carbonates that form relatively large blocks which limit exposure of calcite surfaces to the ambient medium. The association of Pal-CaCO₃ 10% is shown in Figure 6.12.c and 6.12.d. The intimate association of palygorskite fibers with calcite crystals is clearly seen in these photographs. Palygorskite fibers cover the calcite surfaces almost entirely, limiting their direct interaction with other reactive components of the medium. Figure 6.12.e presents the association of the minerals in the Mont-CaCO₃ 10% combination.

The BET surface areas of the different mineral combinations are shown in Figure 6.13. The pure sepiolite sample has the largest surface area of about 350 m² g⁻¹, followed by palygorskite with 220 m² g⁻¹, and 100 m² g⁻¹ for montmorillonite. The mixture of calcite and clay minerals sharply decreased the surface area of the pure clays. The close association of clay particles with large calcite crystals, and the aggregation of clay induced by calcite in the mixed system, reduce the surface area of the clay minerals. An increase from 5 to 10% in the proportion of calcite further slightly reduced the surface area of the combination.

When combined with calcite, palygorskite and sepiolite provided a larger surface area than montmorillonite. This confirms the higher dispersability of the fibrous minerals. With their large reactive surface areas, palygorskite and sepiolite seem to enhance the
Figure 6.12. SEM photomicrographs of clay-calcite combinations. a) A pure calcite crystal, b) The original sepiolite sample containing about 50% carbonate impurities. c) and d) The association of Pal-CaCO$_3$ 10%. e) Mont-CaCO$_3$ 10% combination.
availability of phosphate in a carbonatic system. The influence of these fibrous clays was considerably greater than that of montmorillonite under similar conditions.

![Graph showing BET surface area of Clay-CaCO₃ samples.](image)

Figure 6.13. The BET surface area of Clay-CaCO₃ samples.

To study the chemical composition of the P-desorbing solution, the total soluble Si, Al, Ca, Mg, K and Na were measured. The concentrations of dissolved Ca, Si, Al, and Mg in the first P extraction of different clay-CaCO₃ combinations are presented in Figure 6.14.

Calcium showed a relatively high concentration for all combinations, with a maximum of about 25 µg ml⁻¹ in Mont-CaCO₃ and quantities of 16 µg ml⁻¹ for Pal- and 12 µg ml⁻¹ for Sep-CaCO₃. The concentration of Ca²⁺ was negatively correlated with the
total desorbed P of the samples. Following the same trend as calcium, the concentration of aluminum varied sharply among the samples. The Al content of the interacting

Figure 6.14. Dissolved Ca, Si, Al, and Mg in the first P extraction (KCl) of clay-calcite 10% combinations.

electrolyte with Mont-CaCO₃ amounted at about 20 µg ml⁻¹, while it was only 2 µg ml⁻¹ for Pal-CaCO₃, and zero for Sep-CaCO₃ combinations. The total concentrations of silicon and magnesium were also different for different combinations, but showed a positive correlation with the availability of P sorbed by the samples. Magnesium, with a concentration of 3 µg ml⁻¹, was the highest for Sep-CaCO₃ sample followed by Pal-CaCO₃, with 1 µg ml⁻¹, and less than 1 µg ml⁻¹ for Mont-CaCO₃ combinations. The concentration of silicon for Sep-CaCO₃ extraction was higher than that of the other samples, but was similar for the Pal- and Mont-CaCO₃ samples.
With a higher cation exchange capacity than palygorskite and sepiolite, Mont-Ca releases a higher concentration of Ca$^{2+}$ exchanged with K$^+$ in a P desorbing electrolyte. The higher concentration of Ca$^{2+}$ in the solution may induce the formation of low soluble Ca-phosphate complexes that limit the availability of sorbed P in Mont-CaCO$_3$. The high concentration of aluminum in the electrolyte that interacts with Mont-CaCO$_3$ minerals also results in the formation of relatively insoluble Al-phosphate complexes. This may also explain the lower availability of sorbed P in Mont-CaCO$_3$ than in Pal- and Sep-CaCO$_3$ combinations. Since the concentrations of Ca in all samples are relatively high, the role of soluble Al in fixing of phosphates seems to be more significant.

The dissolved silicon and magnesium both originate from the silicate clays in the samples. The presence of these elements in the solution also affects the P sorption/desorption characteristics of their minerals. Silicon has a relatively high affinity for P sorption sites, enhancing the desorbability of sorbed P (Ryden et al., 1987; Pardo and Guadalix, 1990). Magnesium ions are also reported to interfere with the formation of Ca-phosphate complexes (Kuo and Mikkelsen, 1979; Yadav and Paliwal, 1988). This would increase the phosphate availability in the calcium bearing solutions. Showing a positive correlation with total desorbed P in the different samples, the high concentrations of Si and Mg in Sep-CaCO$_3$ suspension may be the main reason for the higher availability of phosphate in this association. The absence of Al in this sample may be another mechanism that lowers the phosphate fixation below that of Pal- and Mont-CaCO$_3$.

6.4. CONCLUSIONS

Carbonates coexist with palygorskite and sepiolite in soils of arid and semiarid regions. In a close association, palygorskite and sepiolite particles that cover the carbonate crystals and likely reduce the carbonate interactions with the soil solution. Therefore, it seems probable that the presence of palygorskite and sepiolite favors the availability of
phosphates in carbonatic systems. This hypothesis was investigated in this part of the study.

In a sequential extraction, the availability of sorbed organic (IHP) and inorganic phosphate (Pi) on different clay-calcite mixtures was examined using different organic ligands as P extractants. The mixtures were palygorskite and sepiolite combined with 5%, and 10% calcite (Pal-CaCO₃, and Sep-CaCO₃). A mixture of montmorillonite-calcite (Mont-CaCO₃) was included in the experiment for comparison. The pure minerals, silicate clays and calcite, were also examined. The availability of sorbed P was investigated by plotting the total desorbed P, Q, against the solution P concentration, I. The Q/I relationship was described by a desorption isotherm that was suggested by Raven and Hossner (1993).

The results revealed that in the presence of calcite, the P sorption of different systems was controlled by this mineral; however, the presence of silicate clays affected the availability of sorbed phosphates. In sorption of inositol hexaphosphate by clay-calcite mixtures, the sorbed P on Pal-CaCO₃ became more available than that of Mont-CaCO₃ and pure calcite. This may be due to the higher content of Al and Ca atoms and lower content of Mg, as well as smaller surface area, of the Mont-CaCO₃ system. The higher contents of Al and Ca increase the affinity of the system for P retention, while the higher amount of Mg and surface area of the mineral seem to favor the availability of sorbed phosphate by the mixture.

The extraction power of different extractants applied in this experiment was in the following order: citric acid>> oxalic acid> succinic acid ≥ KCl ≥ aspartic acid. The higher the number of carboxyl and hydroxyl group in the ligand, the higher the P extraction power.

The Sep-CaCO₃ sample showed a 50% reduction in sorption of inorganic phosphate compared to pure calcite and other mixtures. The availability of sorbed Pi on Sep-CaCO₃ was also much above that of other mineral mixtures, followed by Pal-CaCO₃.
and Mont-CaCO₃. This may be due to the higher surface area of the Pal- and Sep-CaCO₃ systems, which enforce the role of silicate clay in the mixtures. The chemistry of the systems revealed high concentrations of dissolved Ca and Al in Mont-CaCO₃; the Pal- and Sep-CaCO₃ systems contained higher concentrations of dissolved Mg and Si which favor the availability of phosphate in the system. The higher availability of sorbed P on Pal-CaCO₃ and Sep-CaCO₃ systems shows that the presence of these silicate clays may regulate the release of sorbed phosphates in soils of arid and semiarid regions.
CHAPTER 7

MAGNESIUM AND SILICON INDUCED PHOSPHATE AVAILABILITY IN SMECTITE-, PALYGORSKITE-, AND SEPIOLITE-CALCITE SYSTEMS

7.1. INTRODUCTION

Calcite (CaCO₃) is common in arid and semiarid soils world-wide. In the absence of Fe- and Al- oxides, calcite is considered to be the most effective mineral fixing phosphate in the soils. The presence of this mineral induces the formation of Ca-phosphate compounds with a low solubility and consequently decreases the availability of P in calcareous soils. Dissolved magnesium is reported to hamper the P fixing capacity of calcite. The inhibitory effects of Mg on P sorption of pure calcite have been discussed by a large number of scientists (Bischoff, 1968; Martens and Harris, 1970; Ferguson and McCarty, 1971; Ferguson et al., 1973; Marion and Babcock, 1977; Kuo and Mikkelsen, 1979; Yadav et al., 1984; Yadav and Paliwal, 1988). However, quantitative information about the effects of Mg on P sorption of calcite in the presence of silicate clay minerals is lacking.

The silicic acid anion is also known to be strongly competing for phosphate sorption sites on different soil components (Obihara and Russel, 1972; Alvarez et al., 1980; Smyth and Sanchez, 1980; Ryden et al., 1987; Pardo and Guadalix, 1990); however, information on the effect of dissolved Si on sorption of P by calcite is limited.
Soil solutions usually contain notable levels of Mg and Si ions that may interfere with phosphate retention by calcite. The interference is expected to be more pronounced in soils of arid regions with Mg-silicate clays, such as palygorskite and sepiolite that potentially have high amounts of Mg and Si ions (Shadfan et al., 1985; Singer, 1984; 1989).

In this work the phosphate sorption/desorption behavior of silicate clay-calcite systems was examined in the presence of different levels of Mg and Si ions that may be released from silicate clay minerals in soil systems. The work is part of an attempt to contribute to the better management of P in soils of arid regions.

7.2. MATERIALS AND METHODS

7.2.1. Materials

The calcite used in this study was a Fisher laboratory sample (Lot # 793932) and the silicate clay minerals were: montmorillonite (STx-1) and palygorskite (PF1-1), both CMS source clay minerals, and sepiolite from Eskishehir, Turkey. The montmorillonite and sepiolite samples were purified using Jackson's (1979) procedure and the palygorskite sample was purified using 1 N NaOAc buffer at pH 4 as explained in Chapter 3. The clay minerals were then homoionized with 1 N CaCl₂ and the excess salts were removed to EC of 30 µS m⁻¹; they were then freeze-dried. The BET surface area of all minerals and the cation exchange capacity of the silicate clay samples were then determined (Table 7.1).

To quantify the effects of Mg and Si application on P sorption/desorption of silicate clay-calcite systems, 100% calcite, and mixtures of 90% clay + 10% calcite were prepared. The mixtures were: i) montmorillonite-calcite (Mont-CaCO₃), ii) palygorskite-calcite (Pal-CaCO₃), and iii) sepiolite-calcite (Sep-CaCO₃). Stock solutions of MgCl₂ and fused SiO₂ in Na₂CO₃ with a concentration of 100 µg ml⁻¹ were also prepared for the Mg and Si treatments.
Table 7.1. The BET surface area (SSA) and cation exchange capacity (CEC) of minerals used in the study.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Calcite (Fisher)</th>
<th>Montmorillonite (STx-1)</th>
<th>Palygorskite (PF1-1)</th>
<th>Sepiolite (Eskishehir)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>BET SSA</strong></td>
<td>0.8 ±0.1</td>
<td>82±1</td>
<td>222 ± 4</td>
<td>384 ± 7</td>
</tr>
<tr>
<td><strong>CEC</strong></td>
<td>79±2</td>
<td>14±1</td>
<td>11±1</td>
<td></td>
</tr>
</tbody>
</table>

7.2.2. Mineral suspension

A 3.75 g sample (calcite or clay-calcite mixtures) was suspended in about 80 ml deionized water in a 100 ml volumetric flask at room temperature for 48 h. The pH of the suspension was adjusted to 7.4 at 12, 24, and 48 h using a Mettler DL21 automated titrator using 0.05 N HCl. Before the P sorption experiment, the volume of suspension was increased to 150 ml while its EC and pH adjusted at 2 dS m⁻¹ and 7.4, respectively. A 0.05 N KCl solution was used for EC adjustment. To suppress the microbial activity in the suspensions, chloroform was added in the ratio of 1 ml to 1 L of the suspension.

7.2.3. Phosphate adsorption

Adsorption of phosphate in the presence of Mg and silicon ions, was achieved by adding 15 ml of a solution containing the known concentrations of P, Mg, and Si adjusted at pH 7.4 and EC of 2 dS m⁻¹ to 10 ml of the mineral suspension with the same pH and EC. The solid-to-solution ratio was 1/100. The suspension was shaken for 24 h at the constant temperature (24 ±1°C) in a pre-weighed 50 ml Nalgene centrifuge tube. Phosphate sorption saturation of the minerals was adjusted to about 100% of maximum
sorption, based on the previously established sorption isotherms (Chapter 4). Concentrations of Mg and Si in the suspension were adjusted at 0.0, 5.0, and 10.0 \( \mu g \) ml\(^{-1}\). A treatment of Mg+Si with a concentration of 5.0 \( \mu g \) ml\(^{-1}\) for each element was also included in the experiment. The suspension was then centrifuged for 15 min at 20,000 g to obtain a clear solution for P measurements. Phosphorus was determined by the ascorbic acid method (Murphy and Riley, 1962), with the absorbance being read at 720 nm using a Beckman Model DU Spectrophotometer. A similar experiment was performed with P free electrolyte, adjusted at pH 7.4, and EC of 2 dS m\(^{-1}\) as the control. All the samples were examined in duplicate.

7.2.4. Phosphate desorption

The reversibility of sorbed P in the presence of the Mg and Si treatments was examined using KCl and citric acid (2 \( \times \) 10\(^{-3}\) M) as extractants. The pH and EC of the extractants were adjusted to 7.4 and 2 dS m\(^{-1}\), using 0.05 N HCl or NaOH and 0.05 N KCl. Microbial interference was minimized using a few drops of chloroform. In this work a sequential extraction was carried out to perturb the equilibrium in the experimental solutions. To assess the reversibility of sorbed P, the total desorbed P, Q, is plotted against the equilibrium P concentration, I, in the solution. To describe the Q/I relationship, a desorption isotherm suggested by Raven and Hossner (1993) as

\[
Q = a \ I^{-0.1} + b \ \ln(I + 1) + c
\]

was fitted to the experimental data. In this equation the \( a \), \( b \), and \( c \) are fitting factors.

For the P desorption studies, 25 ml of the P extractants, KCl or citric acid with the same Mg and Si levels as in the sorption treatments, were added to the tubes containing 0.25 g of clay samples pre-loaded with phosphate in the P sorption step. The tubes were capped, shaken vigorously by multivortex to bring the clay samples into suspension and
then placed in a rotary shaker and shaken at room temperature (24 ± 1°C). The time period used for each desorption sequence was 24 h. At the end of each time period, the samples were centrifuged for 15 min at 20,000 g and the clear supernatant was removed for P measurement. Then the tubes with the sample residue were weighed, 25 ml of the respective electrolytes were added, and the samples were then vortexed and placed on the rotary shaker. This procedure was repeated for a total of seven extractions.

The tubes containing the samples were weighed after each desorption in order to determine the solution P that was carried over to the next desorption. This amount was then subtracted from the subsequent desorbed P. The P concentrations in successive volumes were measured, then the total P desorbed from the sample was calculated by summing successive removals, as undertaken by Raven and Hossner (1993). The amount of phosphate desorbed from the samples was corrected for that from the control sample that received no phosphate treatment. The chemical analyses of the supernatants and ion speciation (explained later) were also performed for some samples.

7.2.5. Chemistry of P sorption solution

The chemistry of the P sorption solution for different samples was studied by elemental analyses of the electrolytes. In addition to P concentration measurement, the total soluble Si was determined by colorimetry (Black et al., 1965), Al, Ca and Mg by atomic absorption spectrometry, and K and Na by atomic emission spectrometry, using a Perkin Elmer 3100 Atomic Absorption Spectrophotometer. Since chloride and carbonate ions had been introduced into the solution by KCl and Na₂CO₃ salts, the concentrations of these anions were estimated by considering the amounts of K and Na in the solution. The ion speciation was investigated using SOILCHEM, a chemical speciation computer program (Sposito and Coves, 1992).

The chemical data of the P sorption solutions (cations, anions, pH and the ionic strength), as well as some information about the sorbents involved in the reaction (e.g.,
cation exchange capacity (CEC), specific surface area (SSA), and sorption sites density), were entered in the SOILCHEM computer program for a comprehensive speciation of the factors contributing in P sorption.

7.2.5.1. SOILCHEM assessments

The ion-association models are usually used to estimate the forms and concentrations of chemical species from measured total concentrations of all the components and appropriate thermodynamic equilibrium constants (Sposito, 1981; Allison et al., 1991; Kalbasi et al., 1995). In this study SOILCHEM was applied to explain the fate of phosphate introduced to different systems.

The program calculates the speciation based on chemical thermodynamics (Sposito, 1981; Stumm and Morgan, 1981). For each component of the experimental solution, a mole balance equation is set up and thermodynamic equilibrium constants, corrected for ionic strength and, if appropriate, surface charge conditions, are incorporated into the terms of this equation according to the Law of Mass Action. The solution of the set of nonlinear algebra equations that results from the mole balance is applied to all the components simultaneously, ultimately providing the concentration of each dissolved, solid, and adsorbed species in the system under consideration.

7.2.5.2. Input data for SOILCHEM

The program was run for specified values of pH and ionic strength. The ionic strength (Ie) was estimated with the equation (Marion and Babcock, 1976):

\[ \log I_e = -1.841 + 1.009 \log EC \text{ (dS m}^{-1}) \]

in units of mol L\(^{-1}\). Both precipitation and adsorption were allowed, no redox reactions and mixed solids were considered. Metals in the solution were Al\(^{3+}\), Ca\(^{2+}\), Mg\(^{2+}\), K\(^+\), Na\(^+\), and SOH\(_2\)\(^+\) (specific sorption sites of anions). The major ligands were CO\(_3\)^{2-}, Cl\(^-\), PO\(_4\)^{3-}, SiO\(_2\)(OH)\(_2\)^{2-}, XCON\(^-\), XVAR\(^-\) (the constant and variable cation exchange sites)
and SO\(^-\) (specific sorption sites of cations). Surface charge of the clay minerals was based on experimental data and expressed in mol L\(^{-1}\).

For calcite, the sorption sites were assumed to be the surface Ca\(^{2+}\) and CO\(_3^{2-}\), as suggested by Thompson and Pownall (1989). The surface density of these sites was estimated by Moller and Sastri (1974) and Compton and Pritchard (1990) as 8.3 \(\times\) 10\(^{-6}\) mol m\(^{-2}\). On the basis of numerous parameters Compton and Pritchard (1990) estimated that approximately 1% of the surface sites are active. Taking this into account, the P sorption sites of calcite was estimated at 0.8 \(\times\) 10\(^{-7}\) M. The partial pressure of CO\(_2\) is set as atmospheric pressure of 10\(^{-3.52}\) atm.

**7.3. RESULTS AND DISCUSSION**

### 7.3.1. Phosphate sorption of clay-calcite mixtures in the presence of Mg ions.

The P sorption of different clay-calcite combinations in the presence of two magnesium concentrations is illustrated in Figure 7.1. With no Mg in the solution, the three samples showed a relatively similar P sorption capacity of about 10 cmol kg\(^{-1}\). Addition of 5.0 and 10.0 \(\mu\)g ml\(^{-1}\) Mg sharply decreased the P sorption of calcite to less than 1 cmol kg\(^{-1}\). The decrease in P sorption of Pal-CaCO\(_3\) and Mont-CaCO\(_3\) was not that sharp, but both samples experienced a decrease of about 2 cmol kg\(^{-1}\) in their P sorption capacity.

To assess the chemical speciation of the P sorption by clay-calcite systems, the total concentrations of metals and ligands in the equilibrium solutions were determined together with some surface properties of the sorbents in the systems introduced to SOILCHEM. The output summaries of metal and ligand speciation for P sorption solution of Mont-CaCO\(_3\) against pure CaCO\(_3\) in the presence of 0.0 and 10.0 \(\mu\)g ml\(^{-1}\) Mg are
Figure 7.1. Effect of Mg on P sorption of clay-CaCO₃ mineral mixtures.

given in Table 7.2. According to Sposito and Coves (1995), the bound complex was assumed as the available form of both ligand or cation involved, and the solid complex is the summation of different possible solid compounds between the metal and the relevant ligand, up to a maximum of six compounds.

7.3.2. Effect of Mg on P sorption of pure calcite

The chemical speciation data show that the P sorption solutions in different treatments were saturated with respect to Ca-phosphate minerals. Calcium is predicted to have the highest contribution in the complexation of phosphate that was introduced to calcite and clay-calcite samples. This shows that formation of calcium phosphate is the main mechanism immobilizing the soluble phosphate in carbonatic systems. In the pure calcite sample, in a 24 hour sorption period, the solution P is largely depleted by formation of Ca-phosphate precipitates. Based on SOILCHEM prediction, only about 2% of solution P, which is in form of different complexes with K, Na, and H, may stay as
Table 7.2. Predicted percentage distribution of chemical species for P sorption of Mont-CaCO₃ and CaCO₃ in the presence and absence of 10.0 µg ml⁻¹ dissolved Mg.

<table>
<thead>
<tr>
<th>Metal ‡ or ligand</th>
<th>Species</th>
<th>Primary percentage† distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CaCO₃-Mg§</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-Mg</td>
</tr>
<tr>
<td>Free ion</td>
<td></td>
<td>79.4</td>
</tr>
<tr>
<td>Ca</td>
<td>Bound with Cl</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>In solid with PO₄</td>
<td>19.7</td>
</tr>
<tr>
<td></td>
<td>In solid with XCON</td>
<td>---</td>
</tr>
<tr>
<td>Mg</td>
<td>Bound with Cl</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>Bound with PO₄</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>Bound with OH</td>
<td>---</td>
</tr>
<tr>
<td>Al</td>
<td>In solid with SiO₃</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>In solid with OH</td>
<td>---</td>
</tr>
<tr>
<td>SOH₂</td>
<td>Free metal</td>
<td>48.3</td>
</tr>
<tr>
<td></td>
<td>Bound with PO₄</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>Bound with SiO₃</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>Bound with OH</td>
<td>48.3</td>
</tr>
<tr>
<td></td>
<td>In solid with Ca</td>
<td>98.2</td>
</tr>
<tr>
<td></td>
<td>Bound with Ca</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>Bound with Mg</td>
<td>---</td>
</tr>
<tr>
<td>PO₄</td>
<td>Bound with K</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>Bound with Na</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>Bound with SOH₂</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>Bound with H</td>
<td>1.5</td>
</tr>
<tr>
<td>SiO₃</td>
<td>In solid form with Al</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>Bound with SOH₂</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>Bound with H</td>
<td>---</td>
</tr>
</tbody>
</table>

† Values less than 0.1% are not shown.
‡ For brevity, species of Na, K, Cl, CO₃-, and cation sorption sites are not shown.
§ - Mg is for no addition of dissolved Mg and +Mg is for Mg addition of 10.0 µg ml⁻¹.
soluble or available P (Sposito and Coves, 1995) in the system, while about 80% of Ca is still remaining in the solution as free ions.

Addition of 10.0 µg ml⁻¹ Mg sharply reduced the calcite P sorption, hence a high concentration of P was left in the solution after the P sorption period. The introduction of Mg into the solution increased the calcium concentration, which is likely the result of higher calcite dissociation in the presence of Mg ions. According to thermodynamic constants applied in the calculation, the concentration of dissolved P in the presence of Mg²⁺ is high enough to decrease the free Ca ions to less than 2% of total dissolved calcium, while more than 55% of phosphate is remaining in the solution as hydrogen orthophosphates (H₂PO₄⁻ and HPO₄²⁻). The relatively small proportion of solution P that is directly bound by Mg ions is considered a soluble complex. Due to very small surface area of calcite, it seems that the contribution of surface sorption to total P complexation is negligible even though more than 96% of sorption sites are occupied with phosphate ions, due to the high concentration of P in the solution.

The inhibitory effect of Mg on sorption of P by calcite has been reported to be mainly through its interference in the formation of Ca-phosphate complexes. Marion and Babcock (1977) explained that this effect occurs through the substitution of Mg²⁺ for Ca²⁺ in the calcium phosphate and apatite precipitates, which leads to disruption of the crystal lattice by the highly hydrated Mg²⁺. Since the formation of Ca-phosphates was the major contributor to sorption of phosphate (Table 7.2), the inhibitory mechanism would sharply increase the phosphate availability in the calcium-bearing systems.

It is also established that Mg²⁺ inhibits calcite nucleation and that with time this ion is incorporated in the calcite lattice. This may result in the formation of a dolomitic structure at the surfaces of calcite crystals that has a much lower affinity for phosphate sorption (Yadav and Paliwal, 1988; Coale et al., 1994). However, due to the short time scale of experiment and also the very low contribution of surface complexation in total P sorption, this mechanism may not be of major concern.
7.3.3. Effect of Mg on P sorption of clay-calcite mixtures

The P sorption capacity of clay-calcite combinations is almost as high as pure calcite. However, as shown by the speciation results (Table 7.2) the amount of available P in this system is slightly raised to about 4% (bound with different cations), which is twice as much as that of pure calcite under the same conditions. Therefore, one may conclude that, although calcite controls the P sorption of carbonatic systems, the presence of silicate clays increases the phosphate availability of the system over that of pure calcite. This may be due to clay-calcite interactions that increase the solubility of calcite or newly formed Ca-phosphates in the system.

The addition of Mg to clay-calcite systems also decreased the P sorption capacity of the mixture, however, the reduction was not as sharp as that of observed for pure calcite mineral. It seems that the presence of 90% clay in the mixture to some extent buffers the inhibitory effects of Mg on P sorption by calcite in the system. Sorption of Mg on cation exchange sites of silicate clay minerals may be one factor that decreases the activity of this ion in the solution; however, this was not predicted by the speciation. The SOILCHEM estimation showed that the cation exchange sites were totally occupied by Ca\(^{2+}\) and K\(^+\) ions. Another reason that explains the buffering behavior of silicate clays is a sharp increase in the contribution of surface sorption sites in the complexation of dissolved P.

SOILCHEM predicted that the surface sorption sites may complex about 13% of total dissolved P, making them the second major contributor to P retention in the system. Since the surface sorbed P by silicate clays is more easily available to the plant than the precipitates of Ca-phosphates (Brady, 1990), it may be concluded that application of Mg in a clay-calcite mixture favors the retention of P in more available forms. The P sorption behavior of Pal-CaCO\(_3\) was similar to that of Mont-CaCO\(_3\) (Figure 7.1). The Mg concentration in the Pal-CaCO\(_3\) suspension was slightly (about 1 µg ml\(^{-1}\)) higher than that
of Mont-CaCO₃, but it did not cause a detectable difference in the P sorption capacity of the mixture.

The concentration of total dissolved Al was about 20 μg ml⁻¹ in the Mont-CaCO₃ suspension; however, precipitation of Al-phosphates at the pH of experiment (7.4) was not predicted by the calculations. As Table 7.2 shows, the silicate clay systems are saturated with respect to the formation of Al-SiO₃ and Al-OH precipitates. With a high P sorption capacity, the fresh Al precipitates may also play a significant role in retention of phosphates by silicate clay mixtures; however, due to a lack of data on the surface properties of these compounds, their contribution in P sorption was not considered.

7.3.4. Effect of Si addition on P sorption of clay-calcite mixtures.

Figure 7.2 shows that additions of 5.0 and 10.0 μg ml⁻¹ of dissolved Si decreased the P sorption of clay-CaCO₃ combinations to almost the same extent as the Mg treatments. A supply of 5.0 and 10.0 μg ml⁻¹ silicon sharply reduced the sorption of phosphate in pure calcite; however, the effect of this ion on the P sorption capacity of calcite was milder than that of the Mg treatments (Figure 7.1). The total dissolved Ca concentration also increased when silicon was added to the system. Therefore, one may conclude that introduction of silicon ions enhances the solubility both of calcite and the newly formed Ca-P compounds in the system, which results in a higher concentration of P remaining in the solution. The effect of different ligands (e.g., Cl⁻, HCO₃⁻, and SO₄²⁻) on the dissolution of calcite is well known (Yadav et al., 1984). These ligands may enhance the solubility of calcite by forming Ca ion-pair complexes in the solution. Therefore, it seems that the higher solubility of Ca-phosphates and calcite in the presence of Si ions may also be attributed to the same mechanism.

The distribution of chemical species predicted by SOILCHEM for P sorption of clay-CaCO₃ mixtures in the presence of Si showed almost the same pattern as that for Mg
treatment (data not shown). Precipitation of Ca-phosphate compounds is also predicted to be the major P fixing mechanism in the system. The 10.0 \( \mu \text{g ml}^{-1} \) Si treatment increased the concentration of dissolved Si to about twice that of systems treated with Mg. However, the Si/P ratio in the sorbed phase did not show any increase over the values for Mg treated samples presented in Table 7.2. This may show that in a carbonatic system, the addition of Si increases P availability mainly through dissolution of calcite and

![Graph showing the effect of Si on P sorption of clay-CaCO₃ mineral mixtures.](image)

Figure 7.2. Effect of Si on P sorption of clay-CaCO₃ mineral mixtures.

Ca-phosphates rather than replacing phosphate ions in the surface complexes. The 5.0 \( \mu \text{g ml}^{-1} \) of Si+Mg treatment reduced the P sorption of mineral combinations to the same extent as 5.0 \( \mu \text{g ml}^{-1} \) Mg. This may indicate that Mg plays a more effective role than Si on solubility of phosphate in this system.
7.3.5. Sorption of phosphate by sepiolite-CaCO₃ mixture

The dissolved silicon and magnesium in soils that affect the phosphate sorption reactions, may originate from silicate clay structures. To examine this hypothesis, the P sorption of a mixture of 90% sepiolite and 10% calcite (Sep-CaCO₃), but without the Mg and Si treatments, was investigated. Sepiolite is a Mg-bearing silicate clay with relatively low stability that is capable of supplying significant amounts of Mg and Si ions to the soil solution. The P sorption capacity of the Sep-CaCO₃ mixture and pure CaCO₃ is given in Figure 6.7. The Sep-CaCO₃ 10% system showed about 50% reduction of P sorption capacity in comparison with that of calcite. The total dissolved Mg and Si in the P sorption solution were determined as 3 and 7 μg ml⁻¹, respectively, and Al was below detection (Figure 6.14). The lower buffering behavior of sepiolite, compared to montmorillonite may, therefore, be attributed to its lower Al content which reduces the affinity of this mineral for P sorption, while the release of Mg and Si from sepiolite to the solution sharply reduces the P retention capacity of calcite in the mixture.

7.3.6. Mg and Si induced availability of sorbed P by different clay-calcite mixtures

To assess the availability of P sorbed by different mineral mixtures, a sequential extraction was carried out using KCl and 2×10⁻³ M citric acid solutions. The total desorbed P, Q, is plotted against the equilibrium P concentration, I, in the solution. The Q/I relation was described using the Raven and Hossner (1993) desorption isotherm. Concentrations of 0.0, 5.0 and 10.0 μg ml⁻¹ Mg and Si were added to the KCl and citric acid electrolytes as they were applied for P desorption. The extracting solution with a zero concentration of Mg was considered as blank. The effect of Mg addition on the availability of P sorbed by Pal-CaCO₃ is shown in Figure 7.3.
Figure 7.3. Mg induced availability of sorbed P by Pal-CaCO$_3$ using KCl electrolyte.

The increase in Mg concentration from 0.0 to 5.0 and 10.0 $\mu$g ml$^{-1}$ constantly enhanced the amount of P desorbed from the Pal-CaCO$_3$ sample. The total P desorbed for the 10.0 $\mu$g ml$^{-1}$ treatment amounted at about 1.3 cmol kg$^{-1}$ while it reduced to 1.0 and 0.6 $\mu$g ml$^{-1}$ respectively for the 5.0 and 0.0 Mg treatments. The Mont-CaCO$_3$ sample was also examined with the same treatments (Figure 7.4).

The response of the Mont-CaCO$_3$ sample to the 5 $\mu$g ml$^{-1}$ Mg concentration was relatively small. However, the 10.0 $\mu$g ml$^{-1}$ Mg increased the P availability sharply. At low concentration, the Mg cations may be exchanged with other cations on exchange sites of the clay surfaces. At 10.0 $\mu$g ml$^{-1}$, the amount of Mg added is enough to interfere with P sorption reactions. Due to the higher cation exchange capacity of montmorillonite, this phenomenon is more evident for montmorillonite than palygorskite.
Figure 7.4. Mg induced availability of sorbed P by Mont-CaCO₃ using KCl electrolyte.

The effect of Mg and Si on the availability of sorbed P by clay-calcite combinations can also be examined using citric acid as the extractant. The Mg-induced P desorption isotherms of Pal-CaCO₃ in citric acid are presented in Figure 7.5. The Mg treatments also increased the availability of sorbed P in citric acid. However, the increase over the blank solution was less marked than that in KCl electrolyte. This might be due to the relatively high P extracting power of the citrate ligand that over-shadowed the effect of Mg in the treatment. Also, the complexation of Mg ions by the citrate ligand, which was predicted by SOILCHEM, reduces the activity of this ion to participate in P sorption reactions.

The desorption isotherm induced by the higher concentration of Mg initially shows higher desorbed P values, falling below the desorption isotherm of 5.0 μg ml⁻¹ Mg treatment after the second extraction. This may be due to the faster depletion of the sample
in the presence of the high Mg concentration, but the total recovered P seems to be the same for both treatments.

![Graph showing desorbed P vs equilibrium P concentration](image)

Figure 7.5. Effect of Mg on the availability of sorbed P by Pal-CaCO₃ in citric acid.

The Si treatments also increased the availability of sorbed P in both Pal- and Mont-CaCO₃ combinations. The effect of Si on P availability may be explained by the high affinity of the silicate ligand for P sorption sites, as well as its interference through the formation of Ca- and Al-phosphate complexes. The effect of Si treatments on extractability of P sorbed on the Mont-CaCO₃ is illustrated in Figure 7.6. The 10.0 µg ml⁻¹ Si treatment increased the availability of P sorbed by Mont-CaCO₃ mixture. However, the increase with 5.0 µg ml⁻¹ treatment was not as sharp. The general pattern was similar to that of P availability induced by Mg treatments.

The addition of Si also increased the availability of sorbed P in Pal-CaCO₃ mineral mixtures (Figure 7.7). In this sample, however, the effect of the two levels of Si additions was almost the same. To avoid confusion, these curves were not plotted.
Figure 7.6. Effect of Si on availability of sorbed P by Mont-CaCO$_3$ in KCl.

Figure 7.7. Effect of Si on availability of sorbed P by Pal-CaCO$_3$ in KCl.
To examine the effect of both Mg and Si released by a magnesium bearing mineral, the availability of sorbed P on Sep-CaCO₃ minerals was examined in the absence of Mg and Si treatments. Figure 7.8 shows the desorbability of sorbed P on Sep-CaCO₃ in comparison with Mont-CaCO₃ mineral mixtures. The Sep-CaCO₃ provided a relatively high P concentration in the solution, ranging from 5 to 1 μg ml⁻¹, during the course of sequential desorption. More than 80% of total P sorbed by Sep-CaCO₃ was released in seven days of extraction using KCl electrolyte, which far exceeded other mineral mixtures. Sepiolite, as a slow release source of Mg and Si in the mixture, provided a relatively high concentration of these ions in the solution, which gradually dissolves the phosphate precipitates. Application of sepiolite may, therefore, increase the availability of original and applied P compounds in calcareous soils.

![Figure 7.8. Desorption of sorbed P by Sep-CaCO₃ and Mont-CaCO₃ mineral mixtures in KCl.](image)

7.4. CONCLUSIONS

The P sorption capacity of silicate clay-calcite mixtures is controlled by the presence of calcite in the system. The silicate clays, however, seem to enhance the
availability of sorbed phosphate. Addition of 5.0 and 10.0 μg ml⁻¹ of Mg and Si decreased the P sorption capacity of all samples, while the effect on P sorption by pure calcite was much greater than that of clay-calcite mixtures. The Mg and Si treatments also increased the availability of sorbed phosphates. The effect of Mg and Si on P sorption/desorption of clay-calcite mixtures is mostly through the inhibition of Ca-phosphate formation, which seems to be the largest sink for sorbed P in the system.

Chemical speciation models are useful tools to predict and explain the availability of applied phosphate in the system under consideration. However, due to the involvement of several components in the reaction and a lack of thermodynamic data on interactions of these components, the application of the models is of limited value in understanding sorption/desorption processes.

As a slow release source of Mg and Si, sepiolite in the clay-calcite mixture induced a lower P sorption capacity in comparison with other clay-calcite combinations. The availability of sorbed phosphate on sepiolite-calcite was also much higher than those of other combinations. This suggests that presence or application of sepiolite may favor the availability of phosphate in calcareous soils.
CHAPTER 8
SORPTION OF SELECTED CATIONIC AND NEUTRAL ORGANIC MOLECULES ON PALLYGORSKITE AND SEPIOLITE

8.1. INTRODUCTION

Pallygorskite and sepiolite are fibrous silicate clays, the so-called 'special clays', which are used in more than one hundred different applications (Galan, 1996). One of the principal applications of pallygorskite-sepiolite clays involves uses that take advantage of their sorptive characteristics. In many of applications the sorptive characteristics of the clay surfaces are modified using organic cations (Gerstl and Mingelgrin, 1979; Banerjee and Dureja, 1995) or neutral surfactants (Gerstl and Yaron, 1981). The sorption maxima of organic cations exceed the cation exchange capacity (CEC) of these minerals, showing that besides the contribution of CEC, sorption takes place on neutral sites and neutral complexes that formed through sorption of an organic cation on a negative site.

Many studies have concluded that the silanol groups (Si-OH) of pallygorskite and sepiolite, acting as neutral sites, can react directly with organic reagents to form compounds with true covalent bonds between the mineral substrate and the organic reactant (Ruiz-Hitzky and Fripiat, 1976; Casal Piga and Ruiz-Hitzky, 1977; Hermosin and Cornejo 1986). The sorption of organic cations on a negatively charged site that is already neutralized has been discussed by Nir (1986), Margulies et al. (1988) and Rytwo et al. (1995). Organic cation sorption on neutral sites and neutral complexes results in a charge reversal of the surfaces that in turn, alters the sorption characteristics and colloid
behavior of the clays. Using a micro electrophoresis device, Margulies et al. (1988) showed that the clay particles moved to the negative electrode if adsorption of the organic cations was in excess of the CEC. Knowledge of the quantity of different complexes and inversely charged sites provides a better understanding of the colloid behavior that, in turn, leads to the more effective use of the clay in various applications.

This part of the study is an attempt to quantify the contribution of different complexes in the sorption of two organic cations, methylene blue (MB) and crystal violet (CV), by palygorskite and sepiolite. The contribution of the different complexes is assessed by using the Gouy-Chapman solution and modification of a sorption model described by Nir (1986) and Rytwo et al. (1995). The sorption characteristics of palygorskite and sepiolite for neutral organic molecules were also examined by the application of two neutral organic molecules, Triton-X 100 (TX 100) and 15 crown ether 5 (15C5).

8.2. MATERIALS AND METHODS

8.2.1. Materials

The minerals examined in this study were: palygorskite from Florida (CMS source clay minerals PFI-1) and sepiolite from Eskishehir, Turkey. The clay samples were purified using the method described by Kunze and Dixon (1986) and homoionized with 1 M KCl. The excess salts were removed to an EC of 30 μS m⁻¹, and the K-homoionized clays were then freeze-dried. The external specific surface area of the clay minerals was determined using the N₂-BET method with an Autosorb-1 (Quantachrome Corp., NY), and the cation exchange capacity (CEC) was measured using the BaCl₂ extraction method described by Hendershot et al. (1993) (Table 8.1).

Methylene blue (MB) and crystal violet (CV) as chloride salts, together with surfactant Triton-X 100 (TX100) and 15 crown ether 5 (15C5), were obtained from
Aldrich Chemical Company and used as sorbates without further treatment. The chemical structure of these sorbates is illustrated in Figure 8.1.

### 8.2.2. Adsorption Isotherms

A 1% clay/distilled water suspension was prepared and stirred gently overnight. The pH and EC of suspensions were adjusted to 7 and 0.2 dS/m$^{-1}$ before the sorption experiment using 0.05 M HCl or NaOH and 0.05 M KCl, respectively. Ten ml of the clay suspension were placed in a 50-ml polypropylene screw-cap centrifuge tube. Then 25 ml electrolyte contained sorbate, with the same pH and EC as the clay suspension, was added to the tube, while the suspension was being stirred. The sorbate applied provided a concentration range of 0.00 to 1.25 mmol/g clay in the final suspension. All samples were duplicated. Blanks of sorbate adjusted to EC = 0.2 dS/m$^{-1}$ and pH 7 were also run to correct the data.

The tubes were protected from light and placed in a rotary shaker for 3 d at room temperature (24±1°C) to ensure that a pseudo-equilibrium was reached (Hermosin et al., 1993). The pH of the suspensions was measured and reported as the pH of the equilibrium solution. The suspensions were then centrifuged at 20,000 g for 15 min. The supernatants were analyzed after filtering (Millipore, 0.2 µm). The non-adsorbed dye was

<table>
<thead>
<tr>
<th>Mineral</th>
<th>SSA (m² g$^{-1}$)</th>
<th>CEC (cmol$\text{c}$ kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sepiolite</td>
<td>384±7</td>
<td>11±1</td>
</tr>
<tr>
<td>Palygorskite</td>
<td>222±4</td>
<td>14±1</td>
</tr>
</tbody>
</table>

Table 8.1. Surface area and cation exchange capacity of palygorskite and sepiolite.
Figure 8.1. Chemical structure of triton-X 100 (TX100), 15 crown ether 5 (15C5), methylene blue (MB) and crystal violet (CV).
spectroscopically quantified in the filtrate. After dilution, which is especially crucial in MB measurement (Hang and Brindley, 1970), the absorbance was read at 662 nm for MB and 588 nm for CV solutions using a Beckman Model DU Spectrophotometer. The total carbon was measured using a Shimatzu total carbon analyzer Model TOC-5050A as an indicator of the TX100 and 15C5 concentration in the filtrates.

The amounts of sorbed organic cations and neutral compounds were calculated as the difference between the initial and equilibrium concentrations in the respective solutions. The adsorption isotherms for organic cations were obtained by plotting the amounts of sorption (mmol/g) versus the total amount of sorbate added to the system. These isotherms were described by using the intrinsic binding coefficients, as explained below. The adsorption isotherms of neutral organic molecules, TX100 and 15C5, were described using a Langmuir type of equation by which the concentration of neutral sorption sites was estimated. The validity of the models used to describe the sorption data was evaluated based on the values of the determination coefficient (R^2) and mean square of residuals (MSR).

8.2.3. Diffuse reflectance infrared Fourier transform

The clay surfaces were examined by diffuse reflectance Fourier transform infrared (DR-FTIR) spectrometry as suggested by Nguyen et al. (1990). Freeze-dried samples were examined by collecting 80 scans per second with a resolution of 4 cm\(^{-1}\), using a Bio-Rad 3240 SPS microprocessor controlled spectrophotometer (Cambridge, MA, USA). The spectra were compared against the reference spectrum of pure KBr and expressed in percent absorbance units. The spectrum of the homoionized clay was subtracted from that of the organo-clay complex after the sorption reaction to obtain the differential spectrum of the reaction product.
8.2.4. Adsorption modeling

An extension of the model applied by Nir (1984, 1986), Nir et al. (1994) and Rytwo et al. (1995) was used to describe the sorption data. The main elements accounted for in this procedure were:

i) the cations tightly bound to the surface include cations sorbed to the neutral sorption sites in addition to the free and neutralized negative sites,

ii) cations residing in the diffuse double layer,

iii) polymerization of organic cations, and

iv) solution of the Gouy-Chapman equation for a solid/liquid system containing monovalent cations and particles with planar surfaces. The concentrations of sorption sites in the solid/liquid system were included in the calculations with the units of mole L\(^{-1}\) (M).

In the case of monovalent cations, Xi\(^+\), that bind to uniquely charged negative sites, P\(^-\), forming a neutral complex, PXi\(^0\), on a clay surface, the reaction may be described as:

\[
P^- + Xi^+ = PXi^0
\]  \[1\]

In this reaction, the magnitude of the intrinsic binding constant, Ki, is:

\[
Ki = [PXi^0]/[P^-][Xi^+(0)]
\]  \[2\]

where the concentrations are given in units of mol L\(^{-1}\) or molar (M), and the unit of Ki is M\(^{-1}\). The concentration of the cation, Xi\(^+\), at the colloidal surface is [Xi\(^+\)(0)]. If it is assumed that the clay surface is a plane with an evenly distributed negative charge, and if the counter-ions can be considered point charges in a uniform liquid continuum, then the
equilibrium distribution of exchange cations can be described quantitatively using the Boltzmann equation (Van Olphen 1977) as:

\[ X_i^+(0) = X_i^+ \cdot Y(0) Z_i \]  \[ \text{[3]} \]

in which \( X_i^+ \) is the molar concentration of the cation in its monomeric form in the equilibrium solution, \( Z_i \) is the valence of the given ion, and \( Y(0) \) is a parameter defined as:

\[ Y(0) = \exp (- e \cdot \Psi(0)/kT) \]  \[ \text{[4]} \]

where \( e \) is the absolute magnitude of an electronic charge, \( \Psi(0) \) is the surface potential, \( k \) is Boltzmann's constant, and \( T \) is the absolute temperature. For a negatively charged surface, \( Y(0) > 1 \), and the concentration of the cation at the surface, \( X_i^+(0) \), may be significantly larger than \( X_i^+ \). However, if charge reversal occurs, \( \Psi(0) \) is positive and \( Y(0) < 1 \).

Another type of reaction is considered forming a charged complex (\( PX_i^+ \_2^+ \)):

\[ PX_i^0 \_2 + X_i^+ = PX_i^+ \_2 \]  \[ \text{[5]} \]

with a binding coefficient of

\[ K_i = [PXi_2^+]/[PX_i^0][X_i^+(0)] \]  \[ \text{[6]} \]

In the case of cation sorption by neutral sites, another reaction may also be considered forming a charged complex:

\[ N + X_i^+ = NX_i^+ \]  \[ \text{[7]} \]
where the binding constant for this reaction can be defined as

\[ \text{Kn} = \frac{[\text{NXi}^+]/[\text{N}]}{[\text{Xi}^+](0)} \]  

[8]

In a closed system, for a given cation \( i \), the total amount of the cation added to the system, \( Ci \), consists of different proportions of ions adsorbed, residing in the solution and in the double layer regions. Analytical expressions for the latter were given by Nir et al. (1978). If \( Q_1 \) is the excess amount of monovalent cations in the double layer region above their concentration in the solution, the total amount of cation in the system, \( Ci \), is given by:

\[ Ci = \text{Xi}^+ + \text{PXi}^0 + 2 \text{PXi}^+_2 + \text{NXi}^+ + Q_1 \]  

[9]

Some organic cations (e.g., MB) can form dimers, trimers and even higher order of aggregates in solution (Spencer and Sutter, 1979; Cenens and Shoonheydt, 1988). Aggregation of molecules, which may be considered a proportion of added dye, reduces the concentration of monomer, \( \text{Xi}^+ \). The total concentration of primary molecules, \( \text{Xit} \), in solution was given by Nir et al. (1983) as follows:

\[ [\text{Xit}] = \frac{[\text{Xi}]}{(1 - \text{Kag}[\text{Xi}])^2} \]  

[10]

in which \( \text{Kag} \) is the corresponding binding coefficient for aggregation in solution. The \( \text{Kag} \) may be determined from the adsorption spectrum of pure dye in solution. The adsorption of dye dimers or higher order aggregates may be ignored (Rytwo et al., 1991). Dye aggregation is significant when the dye addition exceeds the CEC of the clay, because below the CEC, almost all the dye is adsorbed.

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If formation of $\text{PX}_2^+$ is considered as complexation between a divalent cation and a single negative site, then according to Nir et al. (1994), in the absence of cation binding to the neutral sites, the surface charge density, $\sigma$, is related to $\sigma_0$, the surface charge density when no cation adsorbed to the surface, by

$$\frac{\sigma}{\sigma_0} = \frac{P^- - \sum \text{PX}_2^+}{P^- + \sum \text{PX}_0 + \sum \text{PX}_2^+}$$  \[11\]

The $\sigma_0$ is charge per unit surface area, which is defined as the ratio of the cation exchange capacity (CEC) to the specific surface area (SSA) of the clay. If CEC and SSA are expressed in units of cmol$_c$ kg$^{-1}$ and m$^2$ g$^{-1}$, respectively, the $\sigma_0$ is calculated as 0.96 x CEC/SSA in units of Coulomb m$^{-2}$ (C m$^{-2}$). The $\sigma_0$ corresponds to the total site concentration per unit area, $P_T$, which is the sum of concentrations of all sites, both free and complexed. The actual surface charge density, $\sigma$, depends on the amount of free sites and the charged complex. The positively charged complex decreases the negative value of $\sigma$. The possibility of charge reversal arises when $P^- < \sum \text{PX}_2^+$. In cases where charged complexes due to binding to neutral sites of the mineral also exist, the actual surface charge density, $\sigma$, changes to more positive values, while $\sigma_0$ remains unchanged (Eq.12):

$$\frac{\sigma}{\sigma_0} = \frac{P^- - \sum \text{PX}_2^+ - \sum N\text{Xi}^+}{P^- + \sum \text{PX}_0 + \sum \text{PX}_2^+}$$  \[12\]

The solution for the Gouy-Chapman equation by Delahay (1965) and Nir et al. (1978) for a planar surface gives a relation between the surface charge density, $\sigma$, the Y(0) parameter and the concentrations of ions in solution, as:

$$\sigma = \left[ \sum X_i (Y(0)^2i - 1) \right]^{1/2} / g$$  \[13\]
where according to Nir (1986), \( g = 17 \left[ 80 \times 298/(\varepsilon T) \right]^{1/2} \) in which \( \varepsilon \) is the bulk dielectric constant and \( T \) is the absolute temperature. The surface charge density is given in unit of Coulomb per unit of surface area (C m\(^{-2}\)).

By substitution of equation [3] and considering the binding coefficients, \( X_{i}^+ \) may be calculated from Eq. (9) if the values of \( Y(0), P^{-}, \) and \( N \) are known, and the \( X_{i}^+ \) value may yield \( P^{-}, N \) and \( Y(0) \) values in equations [12] and [13]. This calculation may be done through an iterative procedure. The procedure consists of the following stages:

i) A guess is made for the values of \( Q_{1}, Y(0), [P^{-}], \) and [\( N \)],

ii) the quantity of \( X_{i}^+ \) is calculated using equation [9],

iii) \( Y(0) \) is calculated by knowing that \( Y(0) > 1 \) if \( \sigma \) is negative, and \( Y(0) < 1 \) if the summation of charged complexes exceeds the free sites, \( P^{-}, \)

iv) the concentrations of the complexed sites, \( PX_{i}^{0}, PX_{i}^{+}, \) and \( NX_{i}^{+} \) are calculated,

v) \( P^{-} \) is calculated by subtraction of summation of \( PX_{i}^{0} \) and \( PX_{i}^{+} \) complexes from \( P_{T} \),

total negative sites,

vi) \( N \) is calculated by subtraction of \( NX_{i}^{+} \) from total \( N \) sites, and

vii) \( Q_{1} \) is calculated with the analytical expressions in Nir et al. (1978). The solution concentration is then recalculated and another cycle of calculation of \( Y(0) \) begins.

Steps (ii) to (vii) are iterated and the criterion for convergence is the relative agreement of the values calculated in the previous cycle with those obtained in the current cycle. In case of MB sorption data, equation (10) was also included to correct for the reduction of \( X_{i}^{+} \) due to aggregation of dye molecules. The intrinsic binding coefficients, \( K_{i}, \overline{K_{i}}, \) and \( K_{n} \), may be chosen to provide the best estimation for the sorption data, as suggested by Rytwo et al. (1995) who established \( K_{i} \) and \( \overline{K_{i}} \) in the sorption of acriflavin (AF), MB, and CV on montmorillonite. For the current work, values of \( K_{i} \) and \( \overline{K_{i}} \) are chosen as
those determined for sorption of MB and CV on montmorillonite by Rytwo et al. (1995) to keep the calculation simple, and Kn was estimated only.

8.2.5. Estimation of neutral sorption sites (N) concentration

Assuming that neutral molecules are sorbed only by the neutral sorption sites, the sorption capacity of palygorskite and sepiolite for two neutral compounds, surfactant triton-X 100 and 15 crown ether 5, was examined. The sorption data were described by a Langmuir type isotherm and the sorption maximum was assumed to equal the number of neutral sorption sites. Using this equation the molar concentration of sorbed neutral molecules, \( X \), was described as

\[
X = \frac{K N [C]}{(1 + K [C])}
\]  

[14]

where \([C]\) is the equilibrium molar concentration of free molecules in the solution, \( K \) is the Langmuir constant with a unit of \( M^{-1} \), a measure for the binding strength of the adsorption sites for molecular species, and \( N \) estimates the number of maximum sorption sites in units of \( M \). The model was fitted to the sorption data based on \( R^2 \) and MSR values using NLIN PROC of the SAS program (SAS Institute, 1985).

8.3. RESULTS AND DISCUSSION

8.3.1. Sorption of TX100 and 15 C 5 by palygorskite and sepiolite.

To estimate the quantity of the neutral sorption sites, the sorption of two neutral molecules, TX100 and 15C5, at different concentrations was examined. The justification for this experiment arises from the report given by Aznar et al. (1992) in which the sorption of surfactant TX100 by sepiolite did not replace the exchangeable Mg\textsuperscript{2+} from the clay surfaces. Furthermore in our work, the sorption of TX100 and 15C5 did not
decrease the pH, showing that the neutral molecules, TX100 and 15C5, did not interact with the cation exchange sites. Figure 8.2 shows the equilibrium pH of different suspensions. Sorption of organic cations, MB and CV, decreases the equilibrium pH more than one unit below the initial pH of the suspension, which was set up at 7. This is in accord with Wang et al. (1996) and Aznar et al. (1992) who reported that due to their high binding constants, organic cations such as MB in amounts above the CEC of clay minerals easily replace all inorganic exchangeable cations. The release of exchangeable H⁺ from the clay surfaces decreases the pH of the clay suspension, but in case of neutral molecules, sorption takes place on neutral sorption sites and no decrease in the initial pH of suspension was observed.

![Figure 8.2](image)

**Figure 8.2.** Sorption of neutral and cationic organic molecules and the pH of equilibrium solution.

The molar concentration of sorbed molecules, when compared with the equilibrium concentration of free molecules, follows a Langmuir isotherm. Figure 8.3
illustrates the sorption isotherms for TX100 and 15C5 by palygorskite and sepiolite, respectively. The N, K and statistical values that estimate the sorption of neutral molecules by the two minerals are presented in Table 8.2. The sorption maximum of TX100 for palygorskite is $9.3 \times 10^{-4}$ M, which exceeds the CEC of this mineral by more than a factor of two. The application of this value as $N$, the total concentration of neutral sites, adequately described the sorption of organic cations on neutral sorption sites. The sorption maxima of palygorskite for 15C5 was $4.1 \times 10^{-4}$ M, considerably lower than that of for sorption of TX100. The lower sorption of 15C5 may be due to its molecular size and the orientation of molecules on the clay surfaces.

Sorption of neutral molecules by sepiolite takes place in larger quantities than that of palygorskite, which may be a reflection of the larger surface area of sepiolite. The

![Figure 8.3. Sorption of neutral organic molecules, TX100 and 15C5, by palygorskite and sepiolite.](image)

sorption maximum of TX100 by sepiolite was $1.2 \times 10^{-3}$ M, which surpasses its CEC by about four times. Adsorption of 15C5 by sepiolite was lower than the adsorption of
TX100, although it was still twice as much as the CEC of this mineral. The N value was also best estimated by the sorption maximum of sepiolite for TX100.

8.3.2. Sorption of organic cations

Sorption of organic cations, MB and CV, by palygorskite and sepiolite was modeled to estimate the contribution of different sites involved in sorption processes. In this study, the intrinsic binding constants Ki and $\overline{K}_i$ of both MB and CV in the formation

Table 8.2. N, K, and statistical values describing sorption isotherms of neutral molecules on palygorskite and sepiolite.

<table>
<thead>
<tr>
<th>Clay mineral</th>
<th>Compound</th>
<th>N (M)</th>
<th>K (M$^{-1}$)</th>
<th>R$^2$</th>
<th>MSR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palygorskite</td>
<td>TX-100</td>
<td>9.3x10$^{-4}$</td>
<td>4800</td>
<td>99.75</td>
<td>9.2x10$^{-10}$</td>
</tr>
<tr>
<td></td>
<td>15 C 5</td>
<td>4.1x10$^{-4}$</td>
<td>1060</td>
<td>99.95</td>
<td>2.1x10$^{-10}$</td>
</tr>
<tr>
<td>Sepiolite</td>
<td>TX-100</td>
<td>1.2x10$^{-3}$</td>
<td>3800</td>
<td>99.83</td>
<td>1.5x10$^{-09}$</td>
</tr>
<tr>
<td></td>
<td>15 C 5</td>
<td>7.0x10$^{-4}$</td>
<td>4860</td>
<td>99.75</td>
<td>9.2x10$^{-10}$</td>
</tr>
</tbody>
</table>

of the neutral complex, $\text{PX}^0$, and the charged complex, $\text{PX}^+$, on montmorillonite previously reported by Rytwo et al. (1995) were applied. The logic behind this application was that the cation exchange reaction in different silicate clays may have a similar nature. Sorption of the cations at a lower level of addition, in which the formation of $\text{NX}^+$ is still negligible, was described satisfactorily using these coefficients. Therefore, only $K_n$, the binding constant of charged complex formation on neutral sites, $\text{NX}^+$, was estimated in this work. A $K_n$ of $6x10^6$ M$^{-1}$ provides the best estimate for the total CV sorption of sepiolite with a determination coefficient of 99.50% and MSR of
$1.42\times10^{-4}$ (Table 8.3). This value of $K_n$ was also used to describe the sorption of the cations on neutral sites in other systems. The intrinsic binding constants applied in this study and statistical values evaluating the goodness of the estimations are presented in Table 8.3.

It is noteworthy that the quantities of cations residing in diffuse double layer that were calculated for different amounts of added sorbate were very low, at least three orders of magnitude smaller than the sorbed cations. Therefore, they were not presented as a constituent of total sorbed dye. This may reflect the relatively low concentration of ions in the experimental solution. Also, the high affinity of organic cations to form different clay-dye complexes is another factor that increases the proportion of sorbed cations over those residing in the diffuse double layer.

The contribution of the different complexes in sorption of CV by palygorskite is presented in Figure 8.4. The total sorption of CV by this mineral reached 0.5 mmol g\(^{-1}\), which is 3.6 times as much as the cation exchange capacity (Table 8.1) of this mineral.

Table 8.3. The intrinsic binding constants and statistical values describing sorption of CV and MB on palygorskite and sepiolite.

<table>
<thead>
<tr>
<th>Clay mineral</th>
<th>Compound</th>
<th>$K_i$ (M(^{-1}))</th>
<th>$\bar{K}_i$ (M(^{-1}))</th>
<th>$K_n$ (M(^{-1}))</th>
<th>$R^2$</th>
<th>MSR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palygorskite</td>
<td>CV</td>
<td>$1.0\times10^6$</td>
<td>$8 \times 10^9$</td>
<td>$6 \times 10^6$</td>
<td>99.18</td>
<td>$6.7\times10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>MB</td>
<td>$3.0\times10^8$</td>
<td>$1 \times 10^6$</td>
<td>$6 \times 10^6$</td>
<td>99.31</td>
<td>$1.8\times10^{-5}$</td>
</tr>
<tr>
<td>Sepiolite</td>
<td>CV</td>
<td>$1.0\times10^6$</td>
<td>$8 \times 10^9$</td>
<td>$6 \times 10^6$</td>
<td>99.50</td>
<td>$1.4\times10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>MB</td>
<td>$3.0\times10^8$</td>
<td>$1 \times 10^6$</td>
<td>$6 \times 10^6$</td>
<td>99.43</td>
<td>$3.4\times10^{-5}$</td>
</tr>
</tbody>
</table>
The quantity of CV adsorbed by montmorillonite, as reported by Rytwo et al. (1995), leveled off at close to 200% of the CEC. This suggests that in palygorskite, the neutral sites play a more significant role than montmorillonite in sorption of organic cations. The significance of neutral sorption sites increases with the level of cation addition.

It seems that at levels of addition below the CEC, the contribution of the $\text{NXi}^+$ complex to total sorption is negligible. Due to the relatively high affinity of CV to form the $\text{PXi}_2^+$ complex, the concentration of neutral complex $\text{PXi}^0$ constitutes an insignificant portion of total clay-cation complexes. The amount of sorbed CV was somewhat higher than that of MB for both clay minerals. The higher affinity of this compound to form charged complexes, $\text{PXi}_2^+$, on negative sorption sites may be a factor explaining the higher sorption of this cation, but the main reason seems to be the tendency of MB to form aggregates in the solution, thereby reducing the monomer concentration (Cenes and Shoonheydt, 1988; Rytwo et al., 1995). Rytwo et al. (1991) also reported that CV shows a better diffusion into the clay aggregates that leads to sorption of this cation, even after flocculation of clay particles that may occur due to sorption of cations. Inclusion of equation [9], which accounts for aggregation of MB in the solution, in the iterative procedure, successfully described the lower sorption of MB for both clay minerals. The constant $\text{Kag}$, which shows the tendency of MB molecules to form polymers, was chosen as 5880 M$^{-1}$, which was the value suggested by Bergmann and O'Konski (1963) and also used by Rytwo et al. (1995).

The contribution of neutral sites in sorption of MB by palygorskite is also quite significant, while the neutral complex, $\text{PXi}^0$, forms a relatively large proportion of total sorbed cations (Figure 8.5). Methylene blue seems to form lower concentrations of charge reversal complexes, $\text{PXi}_2^+$, and $\text{NXi}^+$, and therefore, in the case of sorption of MB, the surface potential is expected to be lower than that for the corresponding concentration of added CV. In several studies, MB and/or CV have been used to determine the CEC of silicate clay minerals (Rytwo et al., 1991; Wang et al., 1996).
Considering the results of this work, it seems that MB sorption data would better estimate the CEC of silicate clay minerals than CV.

Formation of different dye-sepiolite complexes is illustrated in Figures 8.6 and 8.7. The CV sorption of sepiolite levels off at close to 0.6 mmol g⁻¹, which is about 4.6 times as much as the cation exchange capacity of this mineral. The contribution of neutral sorption sites at the maximum CV sorbed reaches more than 60% of total sorption. Due to the larger surface area and lower CEC of this mineral compared to palygorskite, the neutral sites play a more important role in sorption processes by sepiolite. Since the binding constant for neutral sites is less than for the charge reversal complex, as PXi₂⁺ (despite the higher sorption capacity of sepiolite for organic cations), the release of sorbed cations is expected to be easier in this mineral than palygorskite. This behavior makes sepiolite a more appropriate carrier for cationic organic molecules. In the case of MB sorption by sepiolite, the contribution of neutral sites reaches about 70% of the total sorption which supports the above view.

8.3.3. Surface potential of clay-dye complexes

As suggested by Nir (1986), using the experimental data, the surface potential of the clay minerals at room temperature and different levels of dye addition was estimated by a simplified form of equation [4] as:

\[
\Psi(0) = -25 \ln[\Psi(0)]
\]

[15]

The calculated values of \(\Psi(0)\) for palygorskite and sepiolite at different levels of MB and CV addition are given in Table 8.4. Charge reversal occurs when the total dye of 0.2 mmol g⁻¹ was added, which exceeds the CEC of palygorskite and sepiolite by about 40% and 60%, respectively. Sorption of CV seemingly induces larger positive values of surface potential which is due to the larger quantities of sorbed CV that are beyond the
Figure 8.4. Contribution of different complexes, $\text{PX}_i^0$, $\text{PX}_i^+\text{X}_2^+$ and $\text{NX}_i^+$ to total CV sorbed by palygorskite.

Figure 8.5. Contribution of different complexes, $\text{PX}_i^0$, $\text{PX}_i^+\text{X}_2^+$ and $\text{NX}_i^+$ to total MB sorbed by palygorskite.
Figure 8.6. Contribution of different complexes, $\text{PX}_1^0$, $\text{PX}_2^+$ and $\text{NX}_1^+$ to total CV sorbed by sepiolite.

Figure 8.7. Contribution of different complexes, $\text{PX}_1^0$, $\text{PX}_2^+$ and $\text{NX}_1^+$ to total MB sorbed by sepiolite.
CEC of the minerals studied. As discussed earlier, the reason for this may be the larger binding coefficient of CV for the formation of charged complex, PXi⁺², as well as the higher concentration of monomer in CV solution.

Table 8.4. Calculated values for surface potential of palygorskite and sepiolite at different levels of methylene blue (MB) or crystal violet (CV) addition.

<table>
<thead>
<tr>
<th>Total Addition (mmol sorbate/g clay)</th>
<th>Surface Potential, Ψ(0) (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pal - MB</td>
</tr>
<tr>
<td>0.05</td>
<td>-129</td>
</tr>
<tr>
<td>0.10</td>
<td>-105</td>
</tr>
<tr>
<td>0.20</td>
<td>97</td>
</tr>
<tr>
<td>0.30</td>
<td>128</td>
</tr>
<tr>
<td>0.40</td>
<td>150</td>
</tr>
<tr>
<td>0.50</td>
<td>161</td>
</tr>
<tr>
<td>0.60</td>
<td>184</td>
</tr>
<tr>
<td>0.75</td>
<td>189</td>
</tr>
<tr>
<td>1.00</td>
<td>192</td>
</tr>
<tr>
<td>1.25</td>
<td>199</td>
</tr>
</tbody>
</table>

* Pal = palygorskite, Sep = sepiolite

At very low levels of dye addition (e.g., 0.05 mmol g⁻¹), however, MB seems to be more efficient at reducing the surface potential of the minerals. The larger Ki value of MB than CV results in the formation of a higher quantity of neutral complex, PXi⁰, which is apparently the main sorption product at low levels of dye addition. This, in turn, results in a higher satisfaction of surface negative charges by MB than CV at this level of dye addition.

The calculated surface potentials also showed larger values for palygorskite than for sepiolite in corresponding conditions. The difference between the two minerals may
be explained by the larger surface area and lower CEC of sepiolite, which results in lower surface charge density and consequently lower surface potential. Palygorskite colloids showed a higher dispersibility than sepiolite during the experiment. However, they consist of larger particles as revealed by surface area data and electron microscopy (Chapter 3). Higher surface potential values may induce more repulsion among the palygorskite colloids, causing the larger dispersability of this mineral.

8.3.4. FTIR spectroscopy of the clay-organic molecule complexes

To understand the sorption mechanisms of neutral and cationic organic molecules, the clay-organic molecule complexes were examined by diffuse reflectance FTIR. The FTIR patterns of pure sepiolite plotted against sepiolite-organic complexes are presented in Figure 8.8 (A, B, C, D). The IR patterns for sorption of neutral molecules TX100 and 15C5 are presented in Figure 8.8. The \( v_{OH} \) band at 3720 cm\(^{-1}\), representing the silanol group (Si-OH) in sepiolite (Ahlrichs et al., 1975), has disappeared due to the sorption of neutral molecules upon saturation of mineral. Similar results were observed by Aznar et al., (1992) in sorption of methylene blue on sepiolite gels. Since the silanol groups are located at the external edges of mineral fibers, they are easily accessible and interact almost totally with the sorbate molecules.

The differential spectra also shows some perturbation of the \( v_{OH} \) 3680 cm\(^{-1}\) band that is related to the OH group attached to octahedral magnesium. Since these bands are mainly located at the interior of crystal blocks, the relative perturbation may be due to physical hindrance by sorbate and involvement of these groups in sorption at sites of crystal defects.

The FTIR spectra of sorbed organic cations, MB and CV (Figure 8.8 B and C), show almost the same pattern as neutral molecules. This suggests that organic cations react with silanol groups by the same mechanism as neutral molecules. Since the neutral
Figure 8.8. FTIR spectra of (a) sepiolite, (b) and (c) sepiolite with different levels of organic compound additions and (d) a differential spectrum of (c) minus (a)
sites are located at the external surfaces of the fibrous clay particles, the external surface area is a major criterion controlling the number of neutral sorption sites and the contribution of these sites in total sorption.

The FTIR spectra of palygorskite (not shown) revealed a sharp band at 3625 cm\(^{-1}\) assigned to \(\nu_{\text{OH}}\) in Al\(_2\)-OH of the octahedral structure (Serna et al., 1977). The presence of Si-OH groups in palygorskite was observed by a very weak shoulder at 3704 cm\(^{-1}\) that was perturbed by sorption of organic molecules. The intensity of the 3625 cm\(^{-1}\) band was also reduced possibly due to physical coverage of particles by sorbates. The low intensity of the Si-OH band in palygorskite indicates fewer edge surfaces or less imperfections than were observed for the sepiolite. The lower specific surface area of this mineral, 220 m\(^2\) g\(^{-1}\), in contrast to 380 m\(^2\) g\(^{-1}\) for sepiolite, also suggests that palygorskite particles have fewer exposed edges.

8.4. CONCLUSIONS

Palygorskite and sepiolite clay minerals are widely used in applications that take advantage of their sorptive characteristics. Sorption of two cationic and two neutral organic compounds on palygorskite and sepiolite was examined. The sorption maxima and the contribution of different sorption sites were compared for the two minerals. A sorption model that considers formation of different complexes described the sorption isotherms of the organic cations on palygorskite and sepiolite. Use of such a model in sorptive applications of the clays may improve understanding of colloid behavior and lead to more efficient use of these minerals.

For both palygorskite and sepiolite, the sorption of organic cations exceeds the cation exchange capacity of minerals. The neutral sorption sites become more important as the sorption approaches its maxima. The sorption maxima of sepiolite, as well as the contribution of neutral sorption sites in the sorption of the organic cations on sepiolite, were larger than those of palygorskite. This shows that sepiolite may be a more
appropriate carrier for organic cations than palygorskite. The calculated values of surface potential for palygorskite were somewhat larger than those for sepiolite which indicates a higher intrinsic surface charge for this mineral. This may explain the larger dispersibility of palygorskite over that of sepiolite in experimental suspensions.
CHAPTER 9
SUMMARY AND CONCLUSIONS

Palygorskite and sepiolite are fibrous silicate clay minerals that are common in soils of arid and semiarid regions. Due to their large surface area and properties of their sorption sites, these clay minerals could play an appreciable role in the agrochemistry of soils in which they are found. However, quantitative information on the specific role of these silicate minerals in soil fertility is limited. Palygorskite and sepiolite are also used in a wide variety of industrial applications. Study of the sorptive behavior of palygorskite and sepiolite may help to improve the management of arid soils from various aspects of fertility and environment. It may also improve some industrial applications of these silicate clay minerals.

In this work, the interactions of palygorskite and sepiolite with two phosphate (P) compounds and some organic molecules were studied. The study of interactions of palygorskite and sepiolite with P compounds focused on the sorption of inositol hexaphosphate (IHP) and sodium orthophosphate (Pi), with respect to sorption isotherms and kinetics of sorption reactions under different surface cation and electrolyte conditions. Since palygorskite and sepiolite commonly occur in carbonatic environments, the P sorption/desorption of these minerals was also investigated in the presence of calcite. The sorption of organic molecules crystal violet (CV), methylene blue (MB), Triton X 100 (TX100), and 15 crown ether 5 (15 C 5) on palygorskite and sepiolite was studied with emphasis on modeling the sorption processes and quantifying the contribution of the different sorption sites.
The P sorption isotherms of palygorskite and sepiolite were described by a modified Langmuir model. The electrical conductivity (EC) of electrolyte increased the P sorption capacity of the minerals, especially at lower levels of EC. The P sorption capacity of Ca-saturated minerals was higher than that of K-saturated minerals. The inorganic P sorption capacity of palygorskite and sepiolite seem to be higher than for other crystalline silicate clays. This may be due to the large external surface area and the dispersability of these silicate clay minerals.

The sorbed P on sepiolite was almost totally desorbable in a KCl electrolyte, which may be due to the absence of Al atoms in the clay structure. The presence of Mg atoms would also lower the affinity of this mineral for P retention. The desorbability of sorbed P on palygorskite was much lower than that of sepiolite. This may also be explained by the difference of the minerals in their Al and Mg content. The inert nature of sepiolite makes this material a good carrier for inorganic phosphate compounds.

The IHP sorption capacity of sepiolite exceeded the P sorption of this mineral by about 30 times, indicating the high affinity of multidentate IHP ligands for the colloid surfaces. Sorption of IHP on palygorskite reached about 60% of the sepiolite sorption capacity, which is related to the lower surface area of palygorskite. The desorbability of sorbed IHP was much lower than that observed for P. The sorbed IHP at low quantities was hardly desorbable, while desorption exponentially increased as IHP sorption exceeds 10 and 15 cmol kg⁻¹ for palygorskite and sepiolite, respectively. This may show the different energy of sorption for successive layers of sorbate build-up on sorbent surfaces. The P sorption of dehydrated palygorskite and sepiolite was also investigated, revealing that while the intracrystalline channels in fibrous structure of these clay minerals were partly involved in P sorption, they cannot accommodate the large organic P molecules.

The kinetics of P sorption reactions on palygorskite and sepiolite were described using a Freundlich type equation. All sorption reactions indicated a multiple kinetic process. There were two rate process in the reaction period. Sepiolite reaches its adsorption maxima
more rapidly than palygorskite and the adsorption over the slow reaction period was negligible. The sorption of IHP was much faster than that of Pi. Close to 50% of IHP sorption is completed in sepiolite within 2 min and then the reaction continues for more than 24 h with a relatively slow speed. This indicates the high accessibility of sorption sites, but as the reaction proceeds, the surface coverage and the IHP concentration in the solution become limiting factors that reduce the rate of the reaction. The higher pH values decreased the speed of P sorption reactions and the P sorption capacity of the minerals. The P sorption reaction in sepiolite was more pH dependent than that of palygorskite. This was confirmed in a titrometry experiment by the higher sorption of OH⁻ on sepiolite surfaces.

The role of palygorskite and sepiolite on sorption/desorption of phosphate in the presence of calcite was also investigated. A montmorillonite-calcite sample was also studied for comparison. The P sorption capacity of silicate clay-calcite is controlled by the presence of calcite in the mixture. However, the silicate clay seems to increase the availability of sorbed phosphate.

In pure clay systems, the availability of sorbed P on sepiolite was higher than that of palygorskite, which was far above that of montmorillonite. In mixtures of clay and calcite, the availability of IHP sorbed on palygorskite-calcite was higher than that of a montmorillonite-calcite mixture, while the desorbability of IHP sorbed on this mixture was similar to that of pure calcite.

The sorption of Pi was controlled mainly by calcite in the mineral mixtures; however, the presence of silicate clays slightly reduced the P sorption capacity of the mixture below that of pure calcite. Sepiolite was a more effective clay in this regard, causing a 50% reduction in Pi sorption capacity of pure calcite. The availability of sorbed Pi on sepiolite-calcite was much higher than that of other mixtures, followed by those of palygorskite-calcite, montmorillonite-calcite and pure calcite. About 90% of total Pi sorbed on sepiolite-calcite mixture was recovered over seven extractions, while the percent recovery of sorbed Pi was about 25%, 20%, and 5% for palygorskite-calcite,
montmorillonite-calcite mixtures and pure calcite, respectively. The higher availability of phosphate in mineral mixtures containing sepiolite was attributed to the release of Mg and Si which inhibit the formation of Ca-phosphate precipitates.

The effects of Mg and Si addition on P sorption/desorption of different clay-calcite systems were studied. Addition of Mg and Si at the rates of 5 and 10 μg ml⁻¹ of suspension decreased the P sorption capacity of all samples, while the effect of both on P sorption of pure calcite was more pronounced than for clay-calcite mixtures. The effect of Mg and Si on P sorption/desorption of clay-calcite mixtures is mostly through inhibition of Ca-phosphate formation which seems to be the major mechanism of P sorption by the mineral mixtures.

Application of SOILCHEM, a computer program for chemical speciation, confirmed that formation of Ca-phosphates is the major mechanism immobilizing the soluble P in the clay-calcite systems. Sorbed P on the clay surfaces was predicted to be the second largest contributor in retention of P by the systems. Since the sorbed P on clay surfaces is more labile than Ca-phosphate precipitates, it seems that the presence of silicate clays favors the availability of P in the clay-calcite systems. Formation of Al-phosphates was ruled out by the chemical speciation program. However, the montmorillonite-calcite and palygorskite-calcite systems were saturated with respect to Al-silicate compounds. The newly formed Al-silicates may contribute greatly in the retention of phosphate, especially in the montmorillonite-calcite system where the concentration of dissolved Al is relatively high. Due to lack of thermodynamic data on these solids, their contribution in P retention could not be estimated by the chemical speciation program.

As a slow release source of Mg and Si, sepiolite in the clay-calcite mixture induced a lower P sorption capacity compared to other clay-calcite combinations. The availability of sorbed phosphate on sepiolite-calcite was also much higher than that of other combinations. This suggests that the presence or application of sepiolite in calcareous soils may favor the availability of phosphates in the system.
Palygorskite and sepiolite show a high sorption capacity for organic molecules. Adsorption of two organic cations, methylene blue (MB) and crystal violet (CV), by palygorskite and sepiolite was examined, while the quantity of neutral sorption sites of the minerals was estimated by sorption of neutral organic molecules, Triton X 100 (TX 100) and 15 crown ether 5 (15 C 5). For both palygorskite and sepiolite, the sorption of organic cations exceeds the cation exchange capacity of the minerals. The sorption of organic cations beyond the CEC of the minerals is attributed to the sorption of cations on neutral sorption sites (N) as well as the negative sites already satisfied with a cation (PXi\(^+\)). The FTIR patterns of clay-organic cation complexes revealed the sorption of organic cations by silanol groups at the edge of fibrous crystals, which accounts for neutral sorption sites.

A sorption model considering the presence of different sorption sites and the Gouy-Chapman equation, described the sorption isotherms of the organic cations on palygorskite and sepiolite. The model estimated the contribution of different sorption sites, as well as the binding coefficient for neutral sites and the surface potential of the clay minerals. The neutral sorption sites become more important as sorption approaches its maximum. At sorption maxima for both palygorskite and sepiolite, the contribution of neutral sites for sorption of organic cations was the highest followed by the PXi\(^+\) sites in case of CV sorption. For sorption of MB, the contribution of cation exchange sites (P\(^-\)) was the second highest. The sorption maxima and the contribution of neutral sorption sites to sorption of the organic cations on sepiolite were larger than those of palygorskite. This shows that sepiolite may be a more appropriate carrier for organic cations than palygorskite.
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