

EFFECT OF KCl AND CaCl₂ AS BACKGROUND ELECTROLYTES ON THE COMPETITIVE ADSORPTION OF GLYPHOSATE AND PHOSPHATE ON GOETHITE

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Abstract—Competitive adsorption between glyphosate and phosphate on goethite was evaluated. The influence of background electrolyte on the adsorption of glyphosate and phosphate was also investigated by using 0.01 M KCl, 0.1 M KCl and 0.01 M CaCl₂ as background electrolytes. Experiments showed that phosphate displaced adsorbed glyphosate from goethite, whereas glyphosate did not displace phosphate. Results also showed that the background electrolyte had a strong effect on phosphate adsorption, but little effect on glyphosate adsorption. Thus, there are differences between the adsorption of glyphosate and phosphate. The study also showed that 0.01 M KCl caused dispersion of goethite, resulting in inefficient filtering, and that phosphate precipitated as calcium phosphates in 0.01 M CaCl₂ background electrolyte solutions. The results suggest that 0.1 M KCl is a more suitable background electrolyte to determine competitive adsorption processes involving glyphosate and phosphate.

Key Words—Adsorption, Background Electrolyte, Competition, Glyphosate, Goethite, Phosphate.

INTRODUCTION

Glyphosate (N-phosphonomethylglycine) is among the most widely used herbicides (Franz *et al.*, 1997). Because glyphosate contains a phosphonic acid moiety and because phosphate competes with glyphosate for adsorption sites, glyphosate has been proposed to adsorb by ligand exchange through the phosphonic acid moiety in a similar way to the adsorption of phosphate (Hance, 1976; Nicholls and Evans, 1991; Piccolo *et al.*, 1992, 1994).

The competition between glyphosate and phosphate for adsorption sites has been known since 1975 (Sprankle *et al.*, 1975a, b). Competition studies suggest that the phosphate concentration is the most important factor in determining the amount of glyphosate sorbed, and that phosphate in some cases is able to completely desorb glyphosate (Nicholls and Evans, 1991; McBride and Kung, 1989; Hance, 1976; Sprankle *et al.*, 1975a, b). Thus, phosphate may have a crucial influence on the environmental fate of glyphosate.

Despite these results, few attempts, other than the studies listed above, have been made to investigate the competition between glyphosate and phosphate. Additional studies would be useful to predict the behavior of glyphosate and phosphate movement into groundwater. Such studies are also important because of the increasing use of glyphosate (Franz *et al.*, 1997), and because agricultural soils, *e.g.* in Denmark and parts of western Europe, have been fertilized for many years with phosphate in excess of what is absorbed by plants (Del Campillo *et al.*, 1999). Consequently, some soils are so heavily loaded with phosphate that they may not retain surplus glyphosate, thereby leading to groundwater pollution.

The objective of the present study was to evaluate competitive adsorption of glyphosate and phosphate on goethite (α -FeOOH) in different background electrolyte solutions. Goethite was used as a test adsorbent because iron oxides are among the most important phosphate adsorbents, and goethite is the most commonly occurring iron oxide in soils (Borggaard, 1990).

MATERIALS AND METHODS

The glyphosate used in this study was purified from a glyphosate concentrate from Cheminova (Lemvig, Denmark). To 150 mL of glyphosate, 37% hydrochloric acid was added until the pH was \sim 1. The solution was maintained at \sim 4°C for \sim 15 h, which resulted in the precipitation of glyphosate crystals. The crystals were isolated using a filtering flask and Büchner funnel after which the crystals were dissolved in hot triple-distilled water and filtered into an Erlenmeyer flask. Ethanol was added to the glyphosate solution and the sample was stored at 4°C for 2 days. The recrystallization process was repeated and the resulting crystals washed with ethanol and dried in a desiccator. The purity of the glyphosate crystals was tested by Fourier transform infrared (FT-IR) analysis (KBr technique on a Perkin Elmer system 2000 FT-IR) and by measuring the C and N contents (in an integrated LECO apparatus).

Goethite (α -FeOOH) was synthesized as described by Schwertmann and Cornell (1991). The product had a surface area of 40 m²g⁻¹ as measured with N₂ by the BET method (Brauner *et al.*, 1938), and a point of zero charge (PZC) of 8. X-ray diffraction (XRD), Mössbauer spectroscopy, and FT-IR analysis showed no

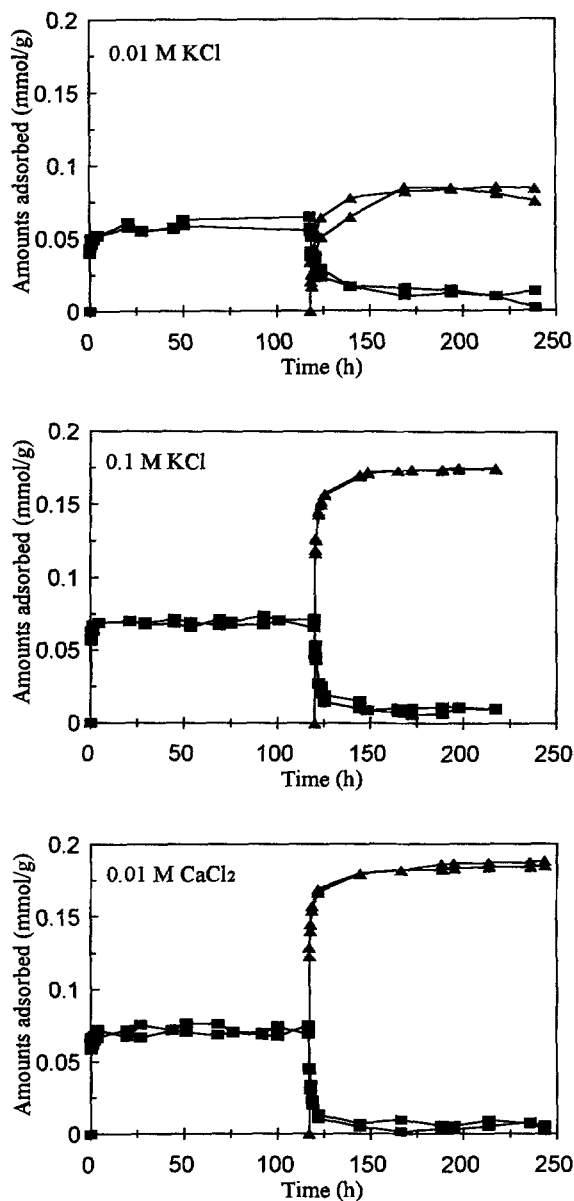


Figure 1. Glyphosate and phosphate competitive adsorption on goethite in 0.01 M KCl, 0.1 M KCl and 0.01 M CaCl_2 . Glyphosate (■) was applied at time 0, and phosphate (▲) was applied after ~120 h.

other mineral phases besides well-crystallized goethite.

Adsorption experiments were conducted by transferring 800 mg of goethite to a glass bottle and adding 381.5 mL of background electrolyte and 16 mL of 2.5% NaN_3 (sodium azide) solution. The azide was added to prevent microbial growth. Either 0.01 M KCl, 0.1 M KCl or 0.01 M CaCl_2 was used as the background electrolyte. The sample pH was adjusted to 7.0 by addition of KOH or HCl. At time zero, 2.5 mL of

80 mM glyphosate containing ^{14}C -labeled glyphosate (150 μL ^{14}C -labeled glyphosate solution in 100 mL of 80 mM glyphosate solution) or 80 mM phosphate solution was added to the goethite suspension, which was kept under constant magnetic stirring. For these experiments, ^{14}C -labeled glyphosate (200 $\mu\text{Ci}/\text{mL}$, 55 mCi/mmol) from Amersham Pharmacia Biotech (Hørsholm, Denmark) was used. The glyphosate or phosphate concentration in the reaction bottle was 0.5 mM. This concentration was chosen because adsorption isotherms showed (data not shown) that at this concentration the goethite becomes saturated. To follow the reaction between goethite and phosphate or glyphosate, 5.00 mL suspension aliquots were taken from the reaction bottles and filtered through a 0.45 μm filter. Within 5 h, four to five samples were taken, and for the following days, one or two samples were taken each day. After 5 d, 80 mM glyphosate was added to the reaction bottle with phosphate and 80 mM phosphate was added to the reaction bottle with glyphosate. The added volumes brought the concentration in the bottle to 0.5 mM. Again, samples were taken during the following 5 d.

The glyphosate concentration in the samples was measured by liquid scintillation counting using an OptiPhase 'HiSafe' 2 scintillation cocktail from Wallac (Turku, Finland) (5.00 mL scintillation cocktail to 0.50 mL sample). The measurements were made using a Wallac WinSpectral 1414 Liquid Scintillation Counter. The phosphate was determined by flow injection analysis by the molybdenum blue/stannous chloride method (Ružička and Hansen, 1981; Janse *et al.*, 1983; Tecator, 1983) using a Tecator FIAstar 5010 Analyzer with a 5027 Sampler. The sample was injected into a carrier stream (water) and merged with a second carrier (water) to avoid matrix effects. The combined stream was then mixed with an acidic ammonium molybdate solution to form a heteropoly acid, which was reduced to molybdenum blue by adding acidic stannous chloride in a second stream. The color of the reduced heteropoly acid was measured at 790 nm. Phosphate concentration was determined by peak height evaluation (Tecator, 1983). The experiment was performed twice for each of the three background electrolytes. The amount adsorbed was determined by subtracting the solution concentration after filtration from the total amount added.

RESULTS AND DISCUSSION

Results are presented in Figures 1 and 2 which show the adsorbed amounts of glyphosate and phosphate as a function of time.

The FT-IR analysis of the glyphosate showed all the characteristic glyphosate bands, but no additional bands. The C content was found to be 21.2% (theoretical value, 21.3%) and the N content was 8.24%

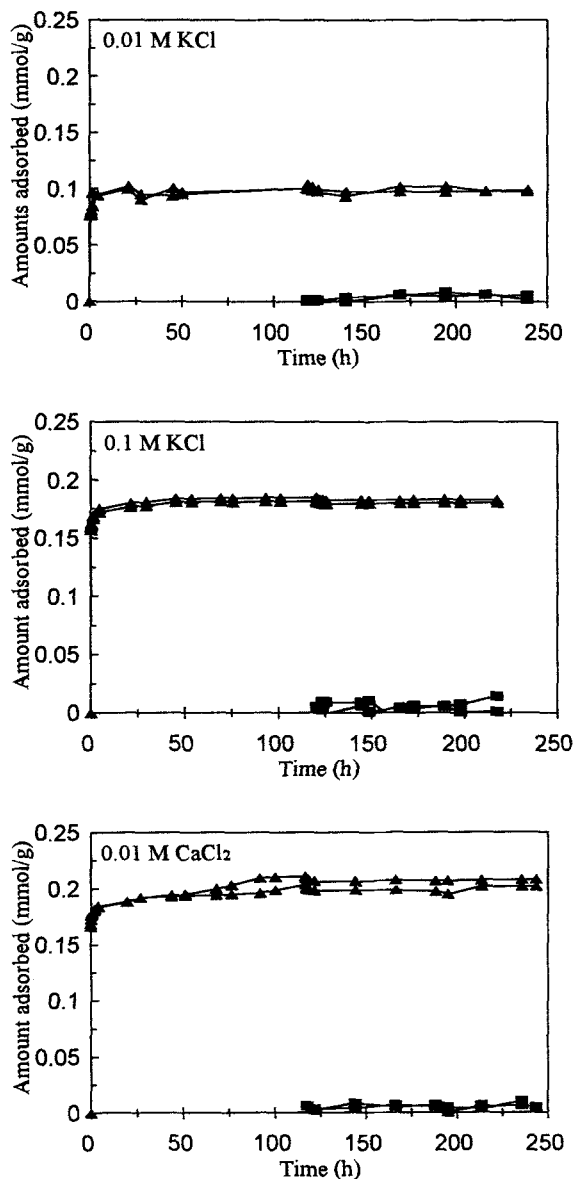


Figure 2. Phosphate and glyphosate competitive adsorption on goethite in 0.01 M KCl, 0.1 M KCl and 0.01 M CaCl₂. Phosphate (▲) was applied at time 0, and glyphosate (■) was applied after ~120 h.

(theoretical value, 8.28%). Both tests suggest that the purified glyphosate was essentially pure.

Adsorption/desorption processes

Adsorption of glyphosate and phosphate alone was observed to be nearly complete within a few hours, indicating that equilibrium was reached. The rapid approach to equilibrium was related to the well crystallized goethite used. For phosphate adsorption on well crystallized goethite, Strauss *et al.* (1997a, b) and Willet *et al.* (1988) found that an adsorption equilibrium

was obtained within 1–3 d. The attainment of adsorption equilibrium indicates that the porosity of the goethite is negligible, and that only surface sites are involved in the adsorption process. The only exception was with phosphate in 0.01 M CaCl₂ electrolyte solutions, where adsorption was initially rapid followed by a slow precipitation reaction. Precipitation of solid calcium phosphates removes phosphate from solution, thus giving the appearance that adsorption is still taking place. Calculations provided by MINTEQA2 (Allison *et al.*, 1991) showed that the solubility products of several calcium phosphates [CaHPO₄·2H₂O, CaHPO₄, Ca₈H₂(PO₄)₆·5H₂O and Ca₁₀(OH)₂(PO₄)₆] were exceeded. The 0.01 M CaCl₂ was used as a background electrolyte in this study because it is a widely used standard background electrolyte (van Lierop, 1990; Nicholls and Evans, 1991; Piccolo *et al.*, 1992, 1996).

The ligand-exchange reaction, which occurs when phosphate is added to a suspension containing glyphosate adsorbed on goethite (Figure 1) is also a fast process, but longer times are required before equilibrium is reached. Slower adsorption of phosphate onto the glyphosate-saturated goethite than onto pure goethite is related to an initial step requiring desorption of glyphosate from the surface. The results suggest that glyphosate was not completely desorbed when phosphate was applied, implying that some of the glyphosate was strongly retained by the goethite.

Amount of glyphosate and phosphate adsorbed

Goethite adsorbed more phosphate than glyphosate in all three background electrolytes (in 0.01 M CaCl₂, the removal of phosphate from solution was related both to adsorption and precipitation, as described above). The amount of phosphate adsorbed was approximately twice the amount of glyphosate adsorbed. This result is probably caused by the difference in the size of the molecules. The glyphosate molecule is 0.43 nm long (Martín *et al.*, 1999) whereas the phosphate molecule is 0.25 nm long (Liu *et al.*, 1999). Thus, glyphosate requires more space than phosphate, thereby reducing the number of adsorption sites available to glyphosate compared to phosphate. Another possible explanation is that glyphosate not only interacts with goethite through the phosphonic acid moiety, but also through the carboxylic acid moiety in a similar way to the adsorption of carboxylic acids (Geelhoed *et al.*, 1998; Liu *et al.*, 1999; Martín *et al.*, 1999). If this is the case, then more surface groups are involved in the adsorption of glyphosate than in the adsorption of phosphate. The amount of glyphosate adsorbed will therefore be less than the amount of adsorbed phosphate.

The amounts of glyphosate and phosphate adsorbed depended on the background electrolyte, and the dependency was much stronger for phosphate than for glyphosate. For glyphosate, the maximum

amounts adsorbed were 0.06 mmol g⁻¹ in 0.01 M KCl, 0.07 mmol g⁻¹ in 0.1 M KCl and 0.07 mmol g⁻¹ in 0.01 M CaCl₂ (Figure 1). For phosphate, the maximum amounts adsorbed were 0.1 mmol g⁻¹ in 0.01 M KCl, 0.18 mmol g⁻¹ in 0.1 M KCl, and 0.21 mmol g⁻¹ in 0.01 M CaCl₂ (Figure 2). The explanation for the greater phosphate removal from CaCl₂ solutions is that phosphate, as described above, also precipitates as calcium phosphates. Moreover, ionic strength also affects adsorption of phosphate as is observed by comparing the adsorption of phosphate in 0.01 M and 0.1 M KCl (Figure 1). Barrow *et al.* (1980), Bolan *et al.* (1986) and He *et al.* (1997) found that there is a pH value below which phosphate adsorption decreases with increasing ionic strength and above which the adsorption increases with increasing ionic strength. This pH value was found to be ~4.5 for phosphate adsorption on goethite (Barrow, 1985). In our study, the pH was 7, and at this pH the adsorption of phosphate increases with increasing ionic strength, as indicated by higher phosphate adsorption in 0.1 M KCl as compared to 0.01 M KCl.

The effect of ionic strength on glyphosate adsorption was small compared to the effect on phosphate adsorption. This result indicates that the adsorption of glyphosate on goethite is different from the adsorption of phosphate. Bolan *et al.* (1986) and He *et al.* (1997) found that the adsorption of phosphate and sulfate was not affected in the same way by a change in ionic strength, and they concluded that this was related to differences in the adsorption mechanisms.

The background electrolyte also affects the amount of glyphosate that can be desorbed by phosphate. When 0.01 M CaCl₂ was used, the desorption of glyphosate is nearly complete, but when 0.01 M and 0.1 M KCl were used there was still a small amount of glyphosate adsorbed after phosphate addition and attainment of equilibrium.

Competition between glyphosate and phosphate

When glyphosate was added to suspensions containing phosphate adsorbed on goethite, only a negligible amount of glyphosate was adsorbed, and there was no change in the amount of phosphate adsorbed (Figure 2). This suggests that when adsorption sites are occupied by phosphate, glyphosate cannot be adsorbed, and glyphosate is unable to desorb phosphate. When phosphate was added to a suspension containing glyphosate adsorbed on goethite, phosphate displaced glyphosate from the adsorption sites, and phosphate was adsorbed (Figure 1). These observations indicate that phosphate is able to desorb glyphosate, whereas glyphosate is unable to desorb phosphate. This was observed for all three background electrolytes. Our results are in accord with those of McBride and Kung (1989) who reported that glyphosate was completely displaced from an amorphous iron oxide by phosphate.

Hingston *et al.* (1968) studied the competition between specifically adsorbed anions and found that "anions are desorbed by competitors only when the competitors can occupy sites in addition to those already occupied by the anion and hence increase the negative charge in the surface". This explanation may account for the capacity of phosphate to desorb glyphosate. In fact, greater amounts of phosphate were adsorbed by goethite (compare initial adsorption in Figures 1 and 2), suggesting that more sites were available to phosphate than to glyphosate. Moreover, this unequal adsorption may also result from the formation of weaker bonds between glyphosate and goethite than between phosphate and goethite. As described above, glyphosate may form bonds both through the phosphonic acid moiety and the carboxylic acid moiety. The bond through the carboxylic acid moiety may resemble the bonds formed by carboxylic acids, such as citric acid. Phosphate can desorb carboxylic acids from goethite (Geelhoed *et al.*, 1998; Liu *et al.*, 1999) and therefore phosphate may possibly break the bond between the carboxylic acid moiety of glyphosate and goethite. The bond through the phosphonic acid moiety of glyphosate is probably different in strength from the bond between phosphate and goethite. The phosphorus in glyphosate is bound to three O atoms and one C atom whereas P in phosphate is bound to four O atoms. Because the electronegativity of C (2.5) differs from the electronegativity of O (3.4), the polarization around the P atom is different in glyphosate from that in phosphate, and this affects the strength of the bond formed with goethite.

The best background electrolyte

Three different background electrolytes (0.01 M KCl, 0.1 M KCl and 0.01 M CaCl₂) were tested in this study. Different background electrolytes were previously employed for adsorption experiments with glyphosate and phosphate: 0.01 M CaCl₂ (Nicholls and Evans, 1991; Piccolo *et al.*, 1992, 1996), 0.5 mM CaCl₂ (Gerritse *et al.*, 1996), 0.01 M NaCl (Morrillo *et al.*, 1997), 0.01 M NaNO₃ (Strauss *et al.*, 1997b), 0.05 M KCl (Madhun *et al.*, 1986) and 0.02 M KCl (Holford and Mattingly, 1975; van Riemsdijk and de Haan, 1981). Two of the background electrolytes (0.01 M KCl and 0.01 M CaCl₂) were problematic and this seriously limits their use in adsorption experiments involving glyphosate and phosphate. The 0.01 M KCl caused dispersion of the goethite. This effect was particularly pronounced for suspensions where glyphosate was applied first and phosphate later. Because of the dispersion, the filtering of the suspension was inefficient, and small goethite particles passed through the 0.45 μm filter. A filter with smaller 0.2 μm pores produced similar results. The presence of particles was verified by measuring the count rate, which is an in-

direct measure of the particle concentration, on a Zetasizer 3000 instrument from Malvern Instruments. The small particles which passed through the filter caused the reaction to continue between phosphate and goethite after filtering. The phosphate concentration in the filtered samples was measured twice with two weeks between measurements. The second measurement showed that the phosphate concentration had decreased, indicating that phosphate continued to react after filtration.

As indicated above, the 0.01 M CaCl₂ solution resulted in phosphate precipitation with calcium, and therefore phosphate either adsorbed or precipitated or both. Thus, 0.1 M KCl is the best choice for a background electrolyte. By using 0.1 M KCl, the ionic strength is sufficiently high that dispersion does not occur, no particles pass the 0.45 µm filter and no precipitation occurs.

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