# Adsorption of paraquat on goethite and humic acid-coated goethite

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## ABSTRACT

Adsorption of cationic pesticides in soils is generally attributed to mineral clays and organic matter components. However, iron oxides may also contribute to such adsorption or affect it by associating with other components. Using goethite and humic acid as models for iron oxides and organic matter respectively, we studied the adsorption of the cationic pesticide paraquat on goethite and humic acid-coated goethite. At pH 4.0 the adsorption on goethite was not significant, and at pH 10.0, although the surface of the oxide was negatively charged, much less pesticide was adsorbed than on mineral clays. At this pH the adsorption of paraquat decreased as the ionic strength increased, and application of the charge distribution multisite complexation model (CD-MUSIC model) enabled interpretation of the results. At pH 4, the adsorption of paraquat on the humic acid-coated goethite was similar to the adsorption on mineral clays, but was considerably less than the adsorption on humic acid in solution. The lower adsorption on solid organic matter is attributed to a decrease in the number of "active" binding sites on the humic acid as a result of the binding to iron oxide.

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## 1. Introduction

The retention and mobility of a pesticide in soil is determined by the sorption/desorption processes, which are governed by the chemical and physical properties of the soils and pesticides involved. The sorption interactions of pesticides in the soil environment may involve either the mineral or organic components, or both. Paraquat is a non-systemic contact herbicide that has been widely used in agriculture for over 50 years [1]. In all types of soils, paraquat is characteristically strongly adsorbed and most of it is thus rendered biologically unavailable. The interaction with different soil components vary, and recent studies [2] have shown that the herbicide has a higher affinity for clay surfaces than for solid soil organic matter. Such interactions are mainly due to the fact that the positively charged paraquat molecules are attracted to the negatively charged minerals and organic matter in soil, so that adsorption at the solid/liquid interface depends on environmental conditions such as pH and ionic strength.

Because of the complexity of natural systems, characterization of the interactions of such molecules with soil fractions must be modelled by use of well defined components. Interactions involving divalent organic pesticides, such as paraquat, and clays, as well as the effect of these interactions on the activity and the environmental impact of these herbicides were first studied several years ago [3–5]. More recently, the adsorption of paraquat on montmorillonite [6] and sepiolite [7] was measured experimentally and simulated by a model that considers the formation of neutral and monovalent charged complexes. The binding of paraquat to soil extracted humic and fulvic acids was studied recently [8], and the application of a simple electrostatic model enabled the authors to conclude that the effects of pH and ionic strength on the binding are due to the effects that these parameters have on the charge of humic substances.

Iron oxides are not considered to be relevant for paraquat sorption in soils with neutral or acidic pH because under such conditions the surface is positively charged. However, hydrous iron oxides may contribute to the sorption of paraquat [9] and may also affect the adsorption of paraquat on inter-associated combinations of iron oxide and organic matter. The aims of the present study were therefore: (1) to quantify the adsorption of paraquat on goethite when the surface charge is positive (acid pH) or negative (basic pH), and for different values of ionic strength, (2) to describe the pesticide–iron oxide binding by use of the CD-MUSIC model, (3) to quantify the adsorption of paraquat on goethite coated by a soil extracted humic acid, to enable analysis of the effect of the iron oxide–organic matter association on adsorption of the pesticide.

## 2. Materials and methods

### 2.1. Materials

Paraquat (1,1′-dimethyl-4,4′-bipyridynium ion) was purchased as the dichloride salt from Aldrich. All other reagents used were analytical (p.a.) grade.

Preparation and characterization of the goethite are described elsewhere [10]. A specific surface area of $67.9\,m^2\,g^{-1}$ was determined by the BET-$N_2$ adsorption method. The surface charge was previously determined with acid/base titrations in KCl solution [10], and the PZC of this goethite was 9.4.

Soil humic acid was extracted by using the method recommended by the International Humic Substances Society [11]. A description of the soil and characterization of the acid properties of the humic acid have previously been reported [10].

### 2.2. Paraquat adsorption to goethite

The paraquat–goethite adsorption experiments were carried out in batches, with solid at concentrations of 6 and $12\,g\,L^{-1}$. Preliminary experiments carried out to analyse the pH effect on the PQ adsorption showed that adsorption is negligible at pH values lower than the PZC (see Fig. S1 in Supplementary data). To ensure that adsorption was remarkable, experiments were conducted at pH > PZC. Binding isotherms were obtained for pH 10.5, ionic strengths $8 \times 10^{-3}$ and 0.02 M (with KCl as inert electrolyte) and paraquat concentrations ranging between $1 \times 10^{-5}$ and $6 \times 10^{-4}$ M. The samples were shaken for 96 h to reach equilibrium, and filtered through a $0.45\,\mu m$ cellulose membrane filter (Millipore). Our preliminary experiments ensured that equilibrium was achieved within this time (see Fig. S2 in Supplementary data).

The concentration of paraquat in the supernatant was measured and the quantity of paraquat adsorbed at the surface of goethite was calculated as the difference between the known total concentration and the concentration remaining in the aqueous phase. All experiments were carried out at least in triplicate, to ensure reproducibility.

The equilibrium concentration of the unbound paraquat was determined by HPLC with a Waters 2695 separation module and a Waters 2996 PDA (photodiode array) detector. A Simmetry® $C_{18}$ column, packed with $5\,\mu m$ particles ($150\,mm \times 3.9\,mm$ i.d.), was used at 25 °C. The isocratic separation was carried out at a flow rate of $1\,mL\,min^{-1}$. The injection volume was $40\,\mu L$. An aqueous solution of 25 mM 1-octanesulfonic acid sodium salt monohydrate at pH 3.0, mixed with methanol at a ratio of 40:60 (v:v), was used as the mobile phase. The paraquat was analyzed at 257 nm, the wavelength of maximum absorption.

### 2.3. Paraquat adsorption to coated goethite

Prior to the paraquat adsorption experiments, the adsorption isotherm of HA on goethite was obtained as described previously [10]. Batch experiments were carried out at pH 4, ionic strength $8 \times 10^{-3}$ M in KCl, goethite suspensions of $0.6\,g\,L^{-1}$ and initial HA concentrations ranging between 10 and $200\,mg\,L^{-1}$. The suspensions were shaken for 24 h, and then centrifuged at 6000 rpm. The humic acid concentration in the solution was determined by UV spectroscopy [12] (UV–vis Spectrophotometer Jasco V-350), measuring the absorbance at 360 and 400 nm of samples previously buffered (pH $\cong$ 8.7) with NaHCO$_3$ 0.05 M [13]. Two wavelengths were used to guarantee a precise response either at low (365 nm) and high (400 nm) HA concentrations. The amount of HA adsorbed was calculated by subtracting the measured concentration from the initial amount of added HA. The adsorption plateau, i.e. saturation of the goethite surface, was reached at an added [HA] of $60\,mg\,L^{-1}$, which corresponds to adsorption of 0.08 g HA (g goethite)$^{-1}$ or $1.2\,mg\,HA\,m^{-2}$ (Fig. 1).

The coated goethite was prepared by adding an excess of HA in order to guarantee maximum possible coverage of the metal oxide surface. This suspension was shaken for 24 h at room temperature and centrifuged at 6000 rpm. The sample of HA-coated goethite
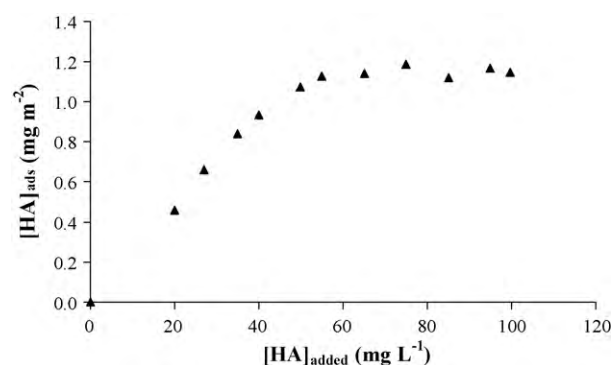


**Fig. 1.** Adsorption isotherm of humic acid on goethite. pH 4, ionic strength = $8 \times 10^{-3}$ M.

was washed with bidistilled water until there was no HA in the supernatant, and was finally freeze-dried.

The binding isotherm of paraquat on HA-coated goethite was obtained for pH 4, ionic strength $8 \times 10^{-3}$ M in KCl, solid concentration in the suspension $3\,g\,L^{-1}$, and concentration of paraquat added in the range between $5 \times 10^{-6}$ and $5 \times 10^{-4}$ M. The experiments were carried out in batches following the same procedure described for adsorption on the bare goethite. Equilibration time for this experiment was also 96 h, once it was verified that longer times (up to 120 h) did not show further adsorption. Nevertheless, since it is expected that equilibrium is controlled by the HA chemistry, shorter times could also be acceptable.

### 2.4. Modelling

Surface complexation models (SCM) describe the adsorption of ions on mineral surfaces and are usually divided into two main parts: one describing the formation reactions of surface species on well defined binding sites and the other one describing the charge distribution and the electrostatic effect of the potential decay in the solid/solution interface.

In this study, the CD-MUSIC model was used to describe the charging and adsorptive behaviour of goethite. Given that a complete description of the model was published by Hiemstra and Van Riemsdijk [14], only a brief description is given here, in which the surface equilibrium and adsorption reactions considered are presented together with some remarks that help the reader understand the main features of the model. In accordance with Hiemstra and Van Riemsdijk [14], the charging behaviour of the goethite at pH 1–11 depends on the protonation/deprotonation reactions of singly coordinated $\equiv FeOH^{-0.5}$ and triply coordinated $\equiv Fe_3O^{-0.5}$ surface groups (Table 1). These reactions are described by the 1 pK model, and the corresponding proton affinity constants ($\log K_H$) were set to equal the experimentally obtained point of zero charge (pH$_{PZC}$) of the goethite.

The salt dependency effect can only be described if ion-pair formation is considered, and therefore it is necessary to include the equilibria between surface charged groups and electrolyte ions (Table 1). The CD model describes the oxide/solution interface as a triple layer (the surface plane or 0-plane, the inner Helmholtz plane or 1-plane and the outer Helmholtz plane or 2-plane), and therefore two capacitance values were required for electrostatic description of the system. Location of the surface complexes in the interface solid/solution and distribution of the charges over the electrostatic planes are prerequisites for application of the model. The electrolyte ions that form ion pairs are positioned in the 2-plane.

In a previous study [8], the proton binding by the HA used in the present work was characterized, and the parameter values that were obtained enabled calculation, for any pH and inert electrolyte

**Table 1**
CD-MUSIC equilibrium surface reactions and model parameters.

| | |
|---|---|
| **Surface protonation reactions** | |
| $FeOH^{-1/2} + H^+ \leftrightarrow FeOH_2^{+1/2}$ | $\log K_{singly} = 9.39$ |
| $Fe_3O^{-1/2} + H^+ \leftrightarrow Fe_3OH^{+1/2}$ | $\log K_{triply} = 9.39$ |
| **Ion-pair formation with electrolyte** | |
| $FeOH^{-1/2} + K^+ \leftrightarrow FeOH^{-1/2} \cdots K^+$ | $\log K_{c,singly} = -0.87$ |
| $FeOH_2^{+1/2} + Cl^- \leftrightarrow FeOH_2^{+1/2} \cdots Cl^-$ | $\log K_{a,singly} = -0.87$ |
| $Fe_3O^{-1/2} + K^+ \leftrightarrow Fe_3O^{-1/2} \cdots K^+$ | $\log K_{c,triply} = -0.87$ |
| $Fe_3OH_2^{+1/2} + Cl^- \leftrightarrow Fe_3OH_2^{+1/2} \cdots Cl^-$ | $\log K_{a,triply} = -0.87$ |
| **Model parameters** | |
| Site density singly ($nm^{-2}$) | 3.45 |
| Site density triply ($nm^{-2}$) | 2.70 |
| Stern layer capacitance, $C$ ($F m^{-2}$) | 0.90 |
| Inner layer capacitance, $C1$ ($F m^{-2}$) | 1.76 |
| Outer layer capacitance, $C2$ ($F m^{-2}$) | 1.86 |
| **Adsorption parameters** | |
| $\log K$ | 2.56 |
| Occupied surface groups (site $nm^{-2}$) | 0.06 |



**Fig. 2.** Adsorption isotherms of paraquat on goethite. [goethite] = 12 g L$^{-1}$, pH 10.5, ionic strength = ($\square$) 0.02 M, ($\triangle$) 8 × 10$^{-3}$ M. The solid lines correspond to the model fit.

concentration, of the negative charge of the humic molecules and the electrostatic potential that this charge generates in the vicinity of the molecules. Adsorption of PQ on HA in solution was also explored in the same study, and the values of the intrinsic parameters that characterize the PQ–HA interactions were obtained. The Donnan model [15] was used to calculate the electrostatic contribution due to the potential generated by the negative charge of the humic acid molecules, and the Langmuir–Freundlich equation was used to calculate the binding parameters:

$$M = M_{max} \frac{(K[PQ])^m}{1 + (K[PQ])^m} \qquad (1)$$

where [PQ] is the concentration of paraquat in the bulk solution, $M$ is the concentration of paraquat bound to the humic substance, $M_{max}$ is the maximum concentration of bound paraquat, $K$ is the paraquat binding constant, and m is the width of the affinity distribution.

In the previous study [8], the values of the conditional binding constants were obtained for the different experimental conditions of pH and inert electrolyte concentration, with the following expression

$$K = K^{int} \exp\left(\frac{-ZF\Psi_D}{RT}\right) \qquad (2)$$

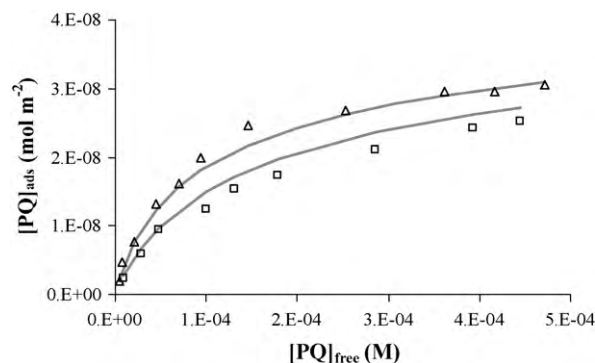where $\Psi_D$ is the electrostatic potential created by the negative charge of the humic acid.

Optimization of the parameters required for describing the experimental binding to both sorbent systems was carried out with the ECOSAT speciation program [16] combined with the FIT program [17].

## 3. Results and discussion

### 3.1. Paraquat adsorption on goethite

The paraquat goethite adsorption data at pH 10.5 are shown in Fig. 2. The correspondence between the results obtained for the two concentrations of the goethite suspension (data for 6 g L$^{-1}$ not shown) indicate that pesticide adsorption does not depend on sorbent concentration.

No adsorption of PQ onto goethite was observed in any of the experiments carried out at pH below PZC (Fig. S1 in Supplementary data). Taking into account these results it can be stated that

in the interaction between PQ and the charged mineral surface the electrostatic effects play an important role. At pH below PZC (pH$_{PZC}$ 9.4) the net surface charge of goethite is positive, and therefore the pesticide cations would be repelled, thus preventing their adsorption on the oxide. In contrast, at pH 10.5 (pH > PZC) some 90% of the surface groups would be ionized, and therefore the net surface charge of goethite would be negative, thus favouring the adsorption process.

The surface concentration of adsorbed paraquat is low since the adsorption isotherm at pH 10.5 displays a plateau at approximately 0.03 μmol m$^{-2}$ (Fig. 2). The only information available about the adsorption of paraquat on mineral surfaces corresponds to clays [6,7,18] at pH values 5–7, at which the surfaces are negatively charged. Adsorption of paraquat is very different for different types of clays, with values of the plateau surface concentration of between 0.18 μmol m$^{-2}$ for silica and 4 μmol m$^{-2}$ for illite; this difference is attributed to the fact that the process of sorption is greatly enhanced in an expanding lattice clay by the ability of the planar paraquat molecules to become intercalated between the lattice layers [1]. The low adsorption of paraquat on goethite is not only due to electrostatic repulsion between adsorbed molecules, and to be adequately explained an adsorption mechanism, for which sufficient bibliographic information is not yet available, would be necessary. These results show that the contribution of iron oxides to the adsorption of paraquat on soils is negligible, and corroborate the conclusion [2] that the extent to which any particular soil adsorbs paraquat will be influenced by the amount and the type of clay minerals present in soil and, to a lesser extent, the amount of soil organic matter.

The adsorption of paraquat depends on the ionic strength, so that as the electrolyte concentration increases, the cationic pesticide adsorption decreases (Fig. 2). The effects of the background electrolyte concentration are usually analyzed in terms of the type of complexes that the adsorbed ions can form with the surface. Ions that form outer-sphere complexes compete with electrolyte ions for adsorption sites, so that a decrease in adsorption is observed when the ionic strength is increased [19].

To describe PQ–goethite binding with the CD-MUSIC model, the nature of the surface complex formed must be known, but the only information available refers to the adsorption of paraquat on the mineral clay surfaces. Rytwo et al. [7] simulated the adsorption of PQ on montmorillonite by use of a model that considered the formation of a complex by the interaction between the paraquat molecule and two negative sites on the surface, and of another complex by the interaction with one negative site. Draoui et al. [18] proposed that for illite, the interaction is mainly electrostatic and the PQ is adsorbed in a flat conformation. The molecular dimensions of PQ, calculated by use of the Gaussian 03 program packages

[20], are 1.08 nm × 0.42 nm, i.e. the molecule covers a surface of 0.45 nm² and may interact in a flat conformation with two negative monocoordinate surface groups of the goethite, as given the density of these type of sites (Table 1), the area corresponding to each is 0.32 nm² per charge. As a result, we considered that the PQ forms surface complexes by the interaction with two negative sites, and that the charge of the organic cation (+2 v.u.) is situated in the 1-plane.

The values of the parameters that describe the charging behaviour of the goethite (Table 1) were determined in a previous study [10] and were taken as fixed values to describe the surface charge while the paraquat–goethite binding data were modelled.

We assumed that only the monocoordinate surface groups (FeOH$^{-0.5}$) take part in the binding [14]. In a preliminary calculation, the density of this type of sites was considered constant, and its value was the same used to interpret the charging behaviour of the goethite surface. Acceptable simulation of the experimental isotherms was not achieved, as none of the values of the adsorption constant produced the apparent saturation observed in the experimental isotherm. In the simulated binding curves, the concentration adsorbed increased continuously and a plateau was not reached, possibly as a consequence of the small fraction of goethite surface covered by the adsorbed PQ molecules.

A new simulation was tested in which the following were maintained the same as in the previous test: (i) the nature of the surface complex formed, (ii) the distribution of charges in the interface layers, and (iii) the parameters used to calculate the contribution of the electrostatic interaction in the formation of the surface complex. Unlike in the previous simulation, in this case, in addition to the adsorption constant, the density of monocoordinate surface groups bound to the molecules of pesticide adsorbed was also considered as an adjustable parameter. This produced good reproduction of the experimental isotherms (Fig. 2) and the values of the intrinsic adsorption parameters were obtained (Table 1).

### 3.2. Paraquat adsorption on HA-coated goethite

At pH 4, the PQ is almost not adsorbed on the goethite, and therefore the pesticide adsorbed on the coated-goethite is bound by the HA. If the value measured for the surface area of the bare goethite is considered as the surface area of the coated goethite, the maximum amount of PQ adsorbed (0.24 μmol m$^{-2}$ i.e. $1.6 \times 10^{-5}$ mol g$^{-1}$) represents a significant amount, similar to the maximum adsorption of the non-expanded lattice clays, which enables us to conclude that in acidic soils the solid organic matter is responsible for the retention of a significant amount of the cationic pesticide.

The adsorption of PQ on HA-coated goethite and on the HA in solution (both expressed per kg of organic matter) are compared in Fig. 3. The amount of pesticide that the HA bound to the surface of the iron oxide adsorbs is approximately 30% of the amount adsorbed by the same weight of HA in solution. This decrease may be interpreted by assuming that some of the reactive sites of the HA adsorbed on the goethite, i.e. of the ionized carboxylic groups, are not available for interacting with the pesticide as they are blocked either because they form chemical bonds with the goethite or because of steric hindrance. In a previous study [8], the binding of PQ was investigated in a solution of the humic acid used in the present study, and the values of the intrinsic binding parameters were therefore available for simulation of the adsorption of PQ on HA-coated goethite. The following steps were carried out: (i) the conditional binding constant was calculated (Eq. (2)), i.e. the value of the constant for pH and ionic strength corresponding to the experimental adsorption isotherm, from the intrinsic constant making use of the Donnan model to correct the contribution of the
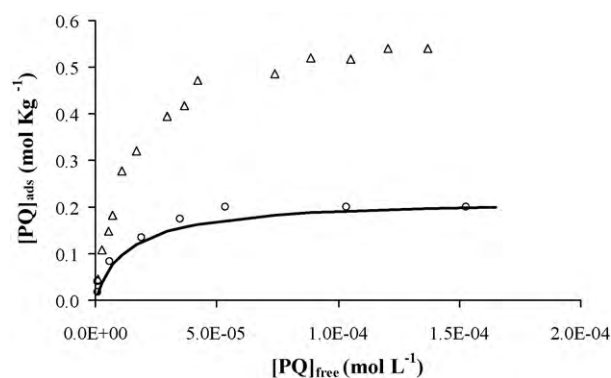


**Fig. 3.** Adsorption of paraquat on humic acid-coated goethite (○) and humic acid in solution (△). pH 4, ionic strength = $8 \times 10^{-3}$ M. The solid line corresponds to the model simulated curve.

electrostatic term [8], (ii) for parameter m in Eq. (1) (i.e. the heterogeneity of the distribution of carboxylic sites), the value obtained for the HA in solution was used, (iii) the maximum number of reactive sites on the HA, i.e. $M_{max}$ in Eq. (1), was considered as a adjustable parameter, (iv) Eq. (1) was used to fit the experimental results for the adsorption of PQ on HA-coated goethite. As shown in Fig. 3, a good fit to the adsorption isotherm was obtained, and the reduction in the maximum density of active binding sites in the "solid" humic acid was consistent with the decrease in adsorption of PQ. It was therefore found that in the humic acid-coated goethite, it is the organic matter that retains the cationic pesticide, because, as seen earlier, at the pH of the experiment (4.0), the adsorption of paraquat on the iron oxide was almost negligible. On the other hand, the adsorption of paraquat on the humic acid that covered the iron oxide was less than on the humic acid in solution, as a result of the lower density of "active" binding sites on the organic matter.

## 4. Conclusions

The adsorption of paraquat on bare goethite was negligible at all pH values below PZC because the surface of the iron oxide was positively charged. At pH above PZC, the goethite surface was negatively charged and adsorption of paraquat was noticeable. The amount of paraquat adsorbed decreased as the ionic strength increased, owing to variation in the electrostatic contribution. These results allow us to conclude that the adsorption of PQ on goethite is mainly controlled by electrostatic interactions.

Even though PQ is adsorbed on goethite surface at high pH values, the surface concentration of adsorbed PQ is rather low (0.03 μmol m$^{-2}$) compared with the values observed for mineral clays surfaces (0.18–4.0 μmol m$^{-2}$). It should be taken into account that clay minerals are better adsorbents for cationic pesticides than iron oxides. Whereas goethite is negatively charged at high pH only, clay minerals exhibit negative charge within the whole pH range.

The analysis of PQ adsorption on the HA-coated goethite reveals a remarkable increase compared to that observed on bare goethite. This result was a priori expected since at acidic pH the organic matter presents high affinity for PQ. Adsorption of paraquat on the "solid" humic acid that covers the goethite was similar to the adsorption on mineral clays, but only 30% of the adsorption on the same organic matter in solution, which can be attributed to a decrease in the number of "active" binding sites of humic acid as a result of their adsorption on the oxide surface.

The overall conclusion is that in acidic soils the solid organic matter is responsible for the retention of a significant amount of the cationic pesticide.

## Acknowledgements

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2010.07.077.

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