The effect of kaolinite on oxalate (bio)degradation at 25°C, and possible implications for adsorption isotherm measurements

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Abstract

Organic compounds derived from agricultural, industrial and domestic waste frequently contaminate soil and ground water. Any attempt to estimate the effect of these organic acids on water quality must include the various interactions between the organic material and the minerals of the host rock and soil. In the present paper, we study the effect of kaolinite surfaces on the degradation rate of oxalate in the presence of microorganisms. The goals are to show that the rate of microbial degradation of organic acids is enhanced in the presence of mineral surface and to evaluate the relative importance of oxalate consumption by microorganism activity vs. (a-biotic) surface catalyzed chemical degradation. We examine both the effect of presence of kaolinite on the rate of oxalate degradation using a flow-through reactor, and oxalate adsorption on the kaolinite surface using a batch reactor. Experiments were conducted at 25°C and 50°C and pH 3. The measurement of the adsorption of organic anions on mineral surfaces is based on change in the organic anion concentration in solution. However, part of this change in concentration may result from degradation of the organic anions, which may be enhanced by microorganism activity.

The change of oxalate concentration on the kaolinite surface as a function of oxalate concentration in solution is described by a general adsorption isotherm:

$$C_s = 8 \times 10^{-7} \frac{20 C_{Ox}^{0.4}}{1 + 20 C_{Ox}^{0.4}}.$$

The decomposition rates in the flow-through experiments ranged from 2×10^{-11} to 2×10^{-10} mol s^{-1}, and depended on the amount of kaolinite present in the cell. Adding an antibiotic mixture to the input solution or increasing the temperature to 50°C halted the oxalate decomposition. Therefore, we conclude that oxalate decomposition at 25°C and pH 3 is controlled by microorganism activity and not by chemical (a-biotic) processes. By adding the same antibiotic mixture to the adsorption experiments, we show that the measurement of oxalate adsorption on the kaolinite surface is not affected by oxalate biodegradation. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Oxalate; Kaolinite; Clay; Adsorption; Decomposition; Organic acid

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1. Introduction

Organic acids are produced in soil by roots of higher plants (Smith, 1976), fungi (Graustein et al., 1977) and bacteria (Berthelin et al., 1974). Smith (1976) studied tree root exudates at Hubbard Brook Experimental Forest, New Hampshire, and found that organic acid release from tree roots was greater than the release of any other organic fraction. Low-molecular-weight organic acids are particularly important because many of them form stable chelates with polyvalent cations (Drever and Vance, 1994). The concentration of these acids in soil solutions is normally less than 1 mM. Fox and Comerford (1990) measured the concentrations of low-molecular-weight organic acids in soil solutions from forest soils. Oxalic acid was found in all samples and was present in the highest concentrations (25–1000 μM).

Organic compounds derived from agricultural, industrial and domestic waste frequently contaminate soil and ground water. Any attempt to estimate the effect of these organic acids on water quality must include the various interactions between the organic material and the minerals of the host rock and soil. Organic matter may have an important effect on the rate of water–rock interaction in different cases, for example: production of secondary porosity in sedimentary basins (Surdam et al., 1984; Huang and Longo, 1992; Giles et al., 1994; Pittman and Hathon, 1994); enhancement of dissolution rate as a result of petroleum contamination of ground water (Hiebert and Bennett, 1992); and enhancement of weathering processes in soils due to the presence of organic material (Berggren and Mulder, 1995).

The content of organic acid in formation water has been extensively studied (see review by Lundegard and Kaharaka, 1994). Commonly, a maximum in concentration is observed at reservoir temperatures between 80°C and 140°C. Thermal decomposition of carboxylic acid is probably the dominant process by which carboxylic acids are destroyed at high temperature. Therefore, a large effort has been made to study the kinetics of organic acid decomposition above 80°C. In some of these studies, it was shown that the decomposition reaction is catalyzed by the surface of the reaction vessel as well as by mineral surfaces (Palmer and Drummond, 1986; Bell and Palmer, 1994; Fein et al., 1995). The relatively

lower concentration of carboxylic acid (< 60 mg/l) at low temperature (< 80°C) is usually explained by bacterial consumption, low generation rate and mixing with surface water (Lundegard and Kaharaka, 1994).

Several studies have examined the effect of a variety of organic acids on the dissolution rates of silicate minerals. The results of some of these studies were summarized by Bennett and Casey (1994), Drever and Vance (1994), Hajash (1994), Stillings et al. (1996, 1998), Oelkers and Schott (1998) and Blake and Walter (1999). Organic complexes with dissolved inorganic ions tend to enhance the solubility of relatively insoluble ions. Some organic acids catalyze both dissolution and precipitation of minerals. However, the mechanisms by which organic substances enhance the dissolution of minerals are difficult to distinguish and are in debate (compare, for example, Oelkers and Schott, 1998; Stillings et al., 1998). Adsorption of an organic ion on a surface site close to the metal may influence the bond strength and thus affect the dissolution rate. For example, an inner-sphere complex with a ligand facilitates the detachment of a central metal ion and enhances the dissolution rate (Stumm, 1992). A simple catalytic reaction mechanism consists of fast adsorption of the organic ion on the mineral surface followed by a slow catalyst-mediated hydrolysis step, which is rate determining. The rate of the hydrolysis depends on the adsorbed surface species. Therefore, the rate law must include the adsorption isotherms of the organic ion. However, only a few of the studies of the effect of organic acids on silicate dissolution measure the adsorption isotherm (e.g., Stillings et al., 1998). Unfortunately, it is currently difficult to directly measure surface concentrations of organic substances. Therefore, the measurements of the adsorption of organic anions on the mineral surface are based on changes in the organic anion concentration in solution. The concentration of the organic anion surface complexes is determined by subtracting the anion concentration of the solution after equilibration from the initial concentration. The problem is that part of this change in concentration may be a result of degradation of the organic anions that may be strongly enhanced by microorganism activity. The purpose of the present paper is to study the effect of kaolinite surfaces in the presence of microorganisms

on the degradation rate of oxalate. In particular, the goals are (1) to show that the rate of microbial degradation of organic acids is enhanced in the presence of mineral surface and (2) to evaluate the relative importance of oxalate consumption by microorganism activity vs. (a-biotic) surface catalyzed chemical degradation. The results of the present study have important implications on understanding both the factors that control the concentrations of low-molecular-weight organic acids in nature and the effect of organic acids on the kinetics of silicates dissolution. The present paper is part of an extensive research on the effect of interactions between organic acids and mineral surfaces on the kinetics of both silicate dissolution and organic acid decomposition. The effect of oxalate on the kinetics of kaolinite dissolution rates will be discussed elsewhere (Cama and Ganor, in preparation). The possible effects of oxalate degradation on the determination of the adsorption of oxalate on kaolinite surface are examined in the present paper in order to determine a reliable adsorption isotherm that would be useful for studying the effect of oxalic acid on kaolinite dissolution rate. In order to ensure that all experiments are conducted under far-from-equilibrium conditions with respect to kaolinite dissolution, all experiments were performed at pH 3. The effect of kaolinite on the rate of oxalate degradation is determined using flow-through reactors, and oxalate adsorption on kaolinite surface is measured using batch reactors.

2. Materials and methods

2.1. Characterization and pretreatment of kaolinite

The kaolinite samples used in this study, KGa-1 and KGa-1B, are source clays of the Clay Mineral Society. These samples are also used to study the effect of oxalate on kaolinite dissolution rate (Cama and Ganor, in preparation), and they have been pretreated in order to obtain reliable stoichiometric dissolution (Nagy et al., 1991; Ganor et al., 1995). Sample KGa-1 was pretreated in 0.001 N $HClO_4$ at 80°C for several months, using the procedure described by Ganor et al. (1995). Sample KGa-1B was pretreated in 0.001 N HNO_3 at 70°C using a similar procedure. All the flow-through experiments were

conducted with sample KGa-1. The batch experiments were conducted with both samples. Some of the batch experiments were conducted with untreated KGa-1B samples.

Samples were degassed in a N_2 atmosphere for 48 h at 135°C. Afterwards, surface area was measured using five-point N_2 adsorption isotherms with a Micromeritics Gemini 2370 surface-area analyzer. The BET-determined initial surface area of pretreated KGa-1, untreated KGa-1B and pretreated KGa-1B were 8.1 ± 0.3, 11.1 ± 0.4 and 10.9 ± 0.4 m^2 g^{-1}, respectively.

2.2. Adsorption measurements

Oxalate adsorption on the kaolinite surface was determined in polyethylene batch reactors fully submersed in a thermostatic bath at 25 ± 0.1°C. Variable amounts of kaolinite and of mixed solution of HNO_3 and oxalate were placed for 2 h in the reactor. In some of the experiments, the samples were mixed using a magnetic stirrer during the entire span of the experiment, whereas in the other experiments, the samples were vigorously shaken during the first 30 s of the experiment, and left unstirred thereafter. After equilibration, the suspension was allowed to settle for a short time. Most of the suspended material was introduced into a syringe and filtered through a Whatman 0.45 μm polyvinylidene fluoride (PVDF) syringe filter and stored in a clean polyethylene bottle. The recovered kaolinite powder was washed through a Millipore 0.45 μm PVDF 47 mm filter, dried, weighed and its surface area was measured.

2.3. Oxalate decomposition experiments

Experiments were carried out using a non-stirred-flow reactor (ca. 35 ml in volume) fully immersed in a water-bath held at constant temperature of 25°C and 50 ± 0.1°C. The reaction cell is a closed cylinder of polycarbonate (Lexan) plastic that contains an inlet line and a filtered outlet line. The cell is composed of two chambers, a lower chamber of 33-mm inner diameter and an upper chamber of 26-mm inner diameter. The two chambers are separated by a fine (5 μm) nylon mesh, on which kaolinite powder was placed. The flow rate was controlled by a peristaltic pump. Solutions were

filtered on the output side of the vessel with a 0.45-µm Durapore membrane (Millipore). In most experiments, steady state was approached within 500 h. After several hundreds to thousand hours at steady state, the experiments were ended. One multi-stage experiment lasted 2800 h.

2.4. Solutions and analyses

Solutions were prepared with a specific oxalate concentration by mixing reagent grade 1 M HNO_3, 0.01 M $Na_2(COO)_2$ and double deionized water (DDW). An antibiotic mixture was added to several of the solutions using a 1/100 volumetric ratio. The antibiotic mixture was prepared by dissolving 100 mg penicillin-G, 50 mg streptomycin, 50 mg ampicillin and 20 mg chloramphenicol (all from Sigma) in 10 ml DDW.

The concentration of oxalate was measured using a Dionex DX-500 Chromatography System with either IonPac AS11A or IonPac AS4A-SC columns. Eluents were prepared from reagent grade sodium hydroxide 50% (w/w) solution (Baker). With the AS11A column, we used a gradient of eluent mixture of 21 mM NaOH and double distilled water (DDW), whereas with AS4A-SC column, we used a constant eluent of 30 mM NaOH. The uncertainty in measured oxalate was usually better than ±1% for concentrations above 25 µM. The precision dropped to ±10% and 15% for measurements below 25 and 5 µM, respectively.

3. Calculations

3.1. Adsorption of oxalate on kaolinite surface

The concentration of oxalate surface complexes is determined by subtracting the oxalate concentration of the solution after equilibration from the initial concentration:

$$C_s = (C_{f,i} - C_{f,e}) \frac{V}{A}, \tag{1}$$

where C_s is the concentration of the oxalate surface complexes (mol m^{-2}), $C_{f,i}$ and $C_{f,e}$ are the initial and equilibrium concentrations of the fluid (mol m^{-3}), respectively, V is the fluid volume (m^3) and

A is the total surface area (m^2). The error in the calculated surface concentration was estimated using a Gaussian error propagation method (Barrante, 1974).

The above calculation is based on the assumptions that oxalate decomposition is negligible during the short period of the adsorption experiments, and that oxalate is not consumed by any other processes. These assumptions are examined in the discussion.

3.2. Oxalate decomposition rate

The change in oxalate concentration with time in a flow-through experiment may be obtained by a simple mass balance equation:

$$\frac{dC}{dt} = -\frac{Rate_{adsor}}{V} - \frac{Rate_{decomp}}{V} + \frac{q}{V}(C_{inp} - C_{out}), \tag{2}$$

where $Rate_{adsor}$ is the rate of oxalate adsorption (mol s^{-1}), $Rate_{decomp}$ is the rate of oxalate decomposition (mol s^{-1}), C_{inp} and C_{out} are the concentrations of oxalate in the input and the output solutions, respectively (mol m^{-3}), t is time (s), V is the volume of the cell (m^3) and q is the fluid volume flux through the system (m^3 s^{-1}). Adsorption on mineral surfaces is a relatively fast process, and is limited by the number of available surface sites. Therefore, after adequate time, the adsorption term in Eq. (2) will approach zero. Thereafter, the oxalate decomposition rate can be calculated based on the change in oxalate concentration according to the expression:

$$Rate_{decomp} = q(C_{inp} - C_{out}) - V\frac{dC}{dt}. \tag{3}$$

The decomposition rate in such an experiment may be readily obtained if steady state is reached, i.e., if the oxalate composition of the solution becomes constant with time ($dC/dt = 0$). In this case, the decomposition rate is balanced by the difference in concentration between input and output solutions:

$$Rate_{decomp} = q(C_{inp} - C_{out}). \tag{4}$$

The error in the calculated rate was estimated using a Gaussian error propagation method (Barrante, 1974).

4. Results and discussion

4.1. Adsorption experiments

Initial and final oxalate concentrations in solution for each batch experiment are shown in Fig. 1. A significant decrease in oxalate concentration is observed between the initial and final oxalate concentrations in solution. Blank experiments (with no mineral) were conducted to verify that the oxalate was not adsorbed by the reactor walls nor affected by the filtration process. No significant change in solution composition was observed in the blank experiments (Fig. 1), and therefore, we suggest that the decrease in oxalate concentration is a result of oxalate adsorption on the kaolinite surface.

By manipulating the length of several experiments, we verify that the duration of the experiments (2 h) is sufficient for equilibration. Fig. 2 shows that the change in concentration occurs during the first 30 min of the experiments. No further change was

Fig. 2. Change in oxalate concentration in solution with time during adsorption experiments. Concentration is decreasing during the first 30 min of the experiments. No further change is observed during the following 3.5 h.
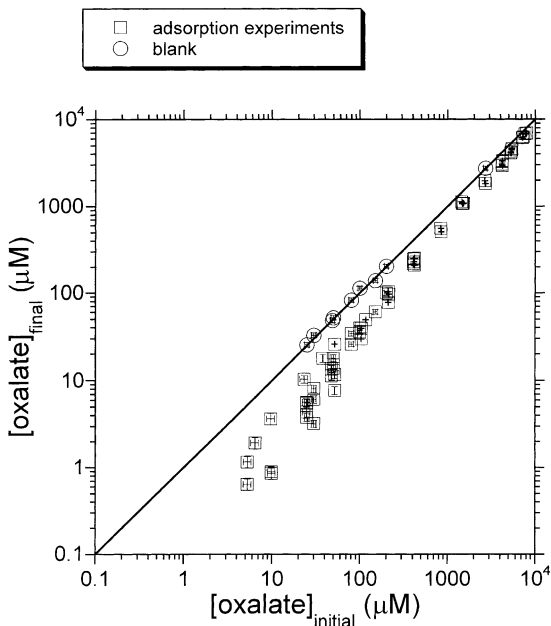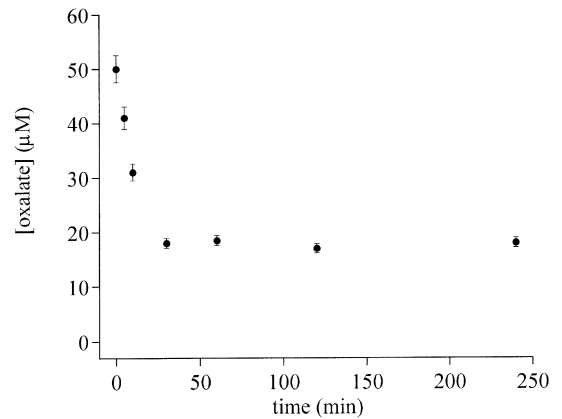

Fig. 1. Initial and final oxalate concentration in the adsorption measurements. The final concentration is lower than the initial concentration as a result of oxalate adsorption. No significant change in solution composition is observed in the blank experiments and therefore, we conclude that the oxalate is adsorbed on the kaolinite surface and not on the reactor walls.

observed during the following 3.5 h. By vigorously shaking the sample for 30 s, we were able to reduce the equilibration time to less than 1 min.

The concentration of the oxalate surface complexes (mol m^{-2}) was calculated using Eq. (1). There is no significant change between the initial and the final BET specific surface area of the kaolinite, and therefore, we used the initial surface area for the calculations. We did not observe any significant differences between the adsorption on the surface of sample KGa-1 and KGa-1B, nor between adsorption on surface of pretreated and untreated samples.

The concentration of an ion (i) chemisorbed on the surface of a mineral may be described by a simple Langmuir adsorption isotherm (Stumm, 1992):

$$C_{i,\mathrm{s}} = F_i \frac{b_i C_i}{1 + b_i C_i}, \tag{5}$$

where $C_{i,\mathrm{s}}$ is the surface concentration of i, F_i is the maximum surface coverage of i, b_i is a coefficient related to the energy of adsorption and C_i is the concentration of i in the solution. For adsorption onto a heterogeneous solid, the energy released during adsorption is usually a nonlinear decreasing function of the surface coverage ($X_{i,\mathrm{ads}}/F_i$), so b_i varies with adsorption energy of sites. By substituting a Gaussian adsorption energy distribution function into the Langmuir model, one obtains an integrated ad-

sorption isotherm of the nonlinear form (Adamson, 1990):

$$C_{i,s} = F_i \frac{b_i C_i^{n_i}}{1 + b_i C_i^{n_i}}. \tag{6}$$

This nonlinear adsorption isotherm reduces to the Freundlich empirical adsorption isotherm at low concentration of i:

$$C_{i,s} = K_i C_i^{n_i}, \tag{7}$$

where K_i is an adsorption coefficient. Both the Freundlich and the Langmuir isotherms are special cases of the general isotherm of Eq. (6).

The change of oxalate concentration on the kaolinite surface as a function of oxalate concentration in solution is shown in Fig. 3. By using a nonlinear regression of Eq. (6), we fitted the experimental data to the general adsorption isotherm (solid line in Fig. 3) and evaluated the maximum surface coverage of

oxalate ($F = 8 \pm 1 \times 10^{-7}$ mol m^{-2}), the b coefficient ($b = 20 \pm 15$ M$^{-0.4}$) and the n coefficient ($n = 0.40 \pm 0.05$). The regression coefficient R^2 equals 0.93. Substituting these values into Eq. (6) yields the adsorption isotherm:

$$C_s = 8 \times 10^{-7} \frac{20 C_{Ox}^{0.4}}{1 + 20 C_{Ox}^{0.4}}, \tag{8}$$

where C_s (mol m^{-2}) is the oxalate surface concentration and C_{Ox} (M) is the concentration of oxalate in the solution. The best-fit curve in Fig. 3 adequately describes the experimental data. However, it is important to note that different combinations of the F and b coefficients yield other curves that adequately describe the experimental data. In other words, the best-fit plot obtained by the regression (Eq. (8)) is not unique, and therefore, the value of the coefficients should be refined using additional experimen-
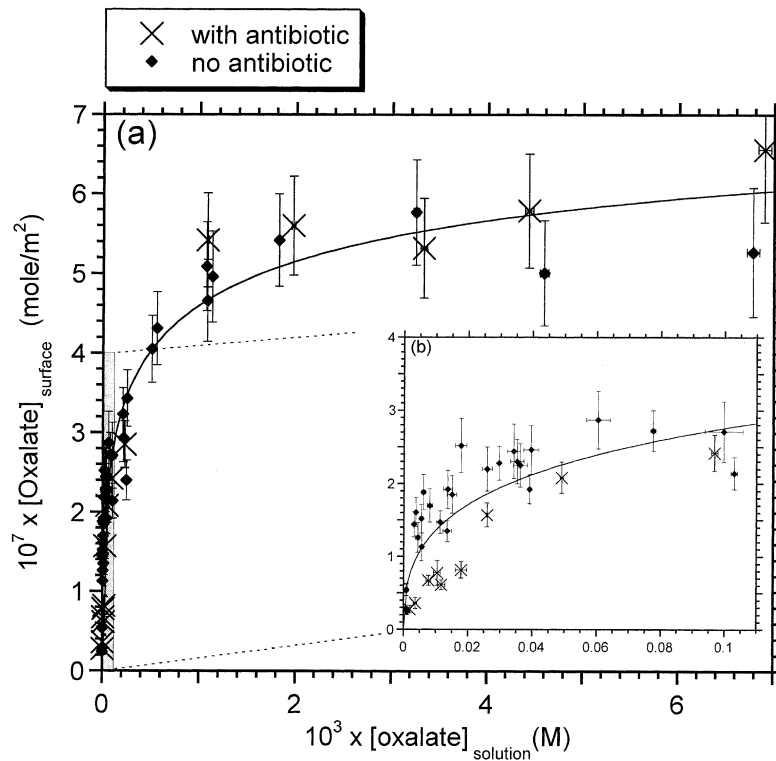

Fig. 3. Adsorption isotherm of oxalate on kaolinite. Enlargement of the low concentration part of the plot (shaded area in (a)) is shown in the insert plot (b). The solid line is a fitting of all the experimental data to the general adsorption isotherm of Eq. (6).

tal data. This point will be further discussed elsewhere (Cama and Ganor, in preparation).

4.2. Oxalate decomposition

As noted above, the calculation of the surface concentration is based on the assumption that oxalate decomposition is negligible during the short period of the adsorption experiments. The blank experiments (Fig. 1) show that in the absence of kaolinite oxalate is neither decomposed nor consumed by any other processes. However, as the adsorption experiments are conducted with kaolinite, it may be argued that part of the change in oxalate concentration is a result of degradation of the organic anions that is either catalyzed by the kaolinite surface (e.g., Palmer and Drummond, 1986; Bell and Palmer, 1994) or enhanced by microorganism activity. To examine this possibility, flow-through experiments were conducted to measure the kinetics of oxalate decomposition in the presence of kaolinite. In order to differentiate between oxalate adsorption and decomposition, we used a flow-through apparatus, in which the rates are determined at steady state, where the concentrations of all the components that affect the reaction rate, including the surface concentration of the organic acid, are constant across time.

A series of flow-through experiments with variable amount of kaolinite and input concentration of 400 μM were conducted to determine the effect of the kaolinite on decomposition rate. The changes in oxalate concentration in each of the flow-through experiments as a function of time are shown in Fig. 4. Average pH and oxalate concentration at steady-state are compiled in Table 1. Input and output

oxalate analyses used to calculate the average steady states are denoted by closed symbols in Fig. 4. The first experiment (Fig. 4a) was composed of two stages. In the first 1150 h, the oxalate input concentration was 100 μM. The output concentration during this stage was < 5 μM. In order to observe oxalate in the output solution, we increased the input oxalate concentration to 400 μM. As a result, oxalate output concentration increased gradually and reached a steady state of 64 ± 8 μM after about 200 h. The decomposition rates in the flow-through experiments (Table 1) ranged from 2×10^{-11} to 2×10^{-10} mol s^{-1}, and they depended on the amount of kaolinite present in the cell. These fast oxalate-decomposition rates may be a result of catalysis by the kaolinite surface or biodegradation. These two possibilities are examined in the following discussion.

4.3. The possible effect of surface catalyzed reaction mechanism on oxalate decomposition

A possible catalytic reaction mechanism for oxalate decomposition in the presence of kaolinite may consist of fast adsorption of the oxalate on the mineral surface followed by a relatively slow surface-mediated oxalate decomposition step. The oxalate-decomposition reaction would therefore be first order with respect to the amount of oxalate adsorbed on the kaolinite surface (a thorough treatment of a similar reaction mechanism can be found in Bell et al., 1994):

$$\frac{dN}{dt} = -k_{kaol} N_s = -k_{kaol} C_s S_r, \qquad (9)$$

where N (mol) is the number of oxalate ions in solution, t is time (s), k_{kaol} (s^{-1}) is a rate coeffi-

Table 1
Experiment conditions and steady state average concentration of the flow-through experiments

| Experiment	Flow rate (ml/min)	Input		Mass (g)	Final Sa[a] (m²/g)	Steady state		Surface oxalate (mol/m²)	Surface oxalate (mol)	Decomposition rate (mol/s)
		pH	Oxalate (μM)			pH	Oxalate[a] (μM)			
kgal-ox-25-1.1	0.040	3.14	395	0.0104	7.50	3.17	361	3.70E − 07	2.9E − 08	2.28E − 11
kgal-ox-25-3.1	0.038	3.19	394	0.0000		3.23	344			3.23E − 11
kgal-ox-25-2.1	0.041	3.14	395	0.0547	7.50	3.20	347	3.66E − 07	1.5E − 07	3.31E − 11
kgal-ox-25-4.1	0.039	3.14	395	0.3006	7.59	3.23	289	3.52E − 07	8.0E − 07	6.89E − 11
kgal-ox-25-5.1	0.039	3.14	396	0.4006	7.69	3.22	281	3.49E − 07	1.1E − 07	7.59E − 11
kgal-ox-25-6.1	0.037	3.14	398	0.4010	7.63	3.25	238	3.36E − 07	1.0E − 06	9.90E − 11
Kgal-25-1M.1	0.039	3.23	398	0.9975	8.50	3.68	66	2.42E − 07	2.0E − 06	2.16E − 10

[a] Final Sa = final specific surface area.
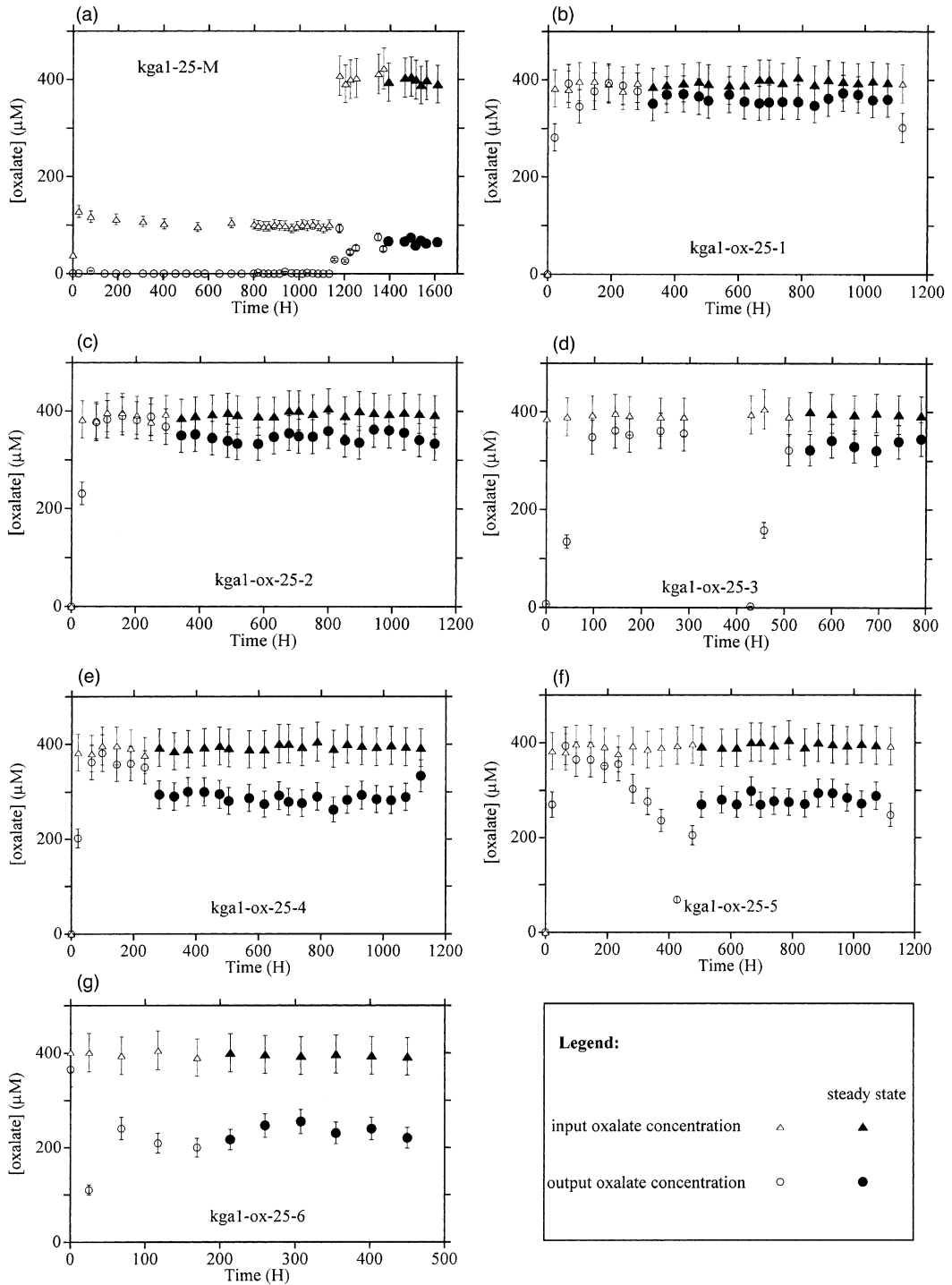
Fig. 4. Variations in oxalate concentration as a function of time in the flow-through experiments. Oxalate analyses used to calculate average steady state are marked by closed symbols.

cient, N_s (mol) is the number of oxalate ions on the surface, C_s (mol m^{-2}) is the oxalate surface concentration and S_r is the total surface area. The rate law of Eq. (9) predicts that the oxalate-decomposition rate is zero in the absence of kaolinite. This is not the case if another reaction mechanism influences the oxalate decomposition. Such oxalate decomposition was observed in experiment kga1-ox-25-3 that was conducted without kaolinite. Therefore, another coefficient, k_0 (mol s^{-1}), should be introduced into the rate law in order to take into account background oxalate decomposition that is not influenced by the presence of kaolinite:

$$\frac{dN}{dt} = -k_0 - k_{kaol}N_s = -k_0 - k_{kaol}C_sS_r. \qquad (10)$$

The above kinetic model explains the fast oxalate decomposition observed in the flow-through experiments by surface catalysis. The model (Eq. (10)) predicts that the rate of oxalate decomposition increases linearly with the amount of oxalate adsorbed on the kaolinite surface, N_s, which is the product of the surface concentration and the total surface area. Fig. 5 plots the rate of oxalate decomposition as a function of N_s. As predicted by the suggested model, the rate increases linearly with the amount of adsorbed oxalate.
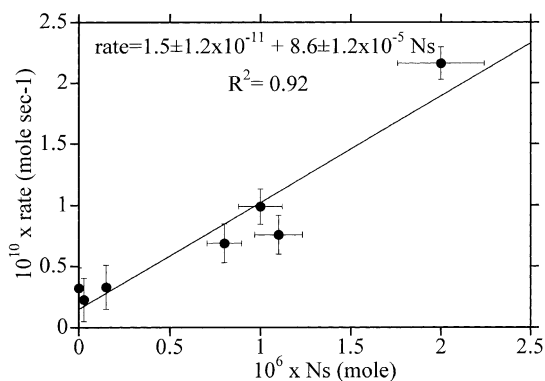

Fig. 5. Oxalate decomposition rate as a function of the number of oxalate ions on the kaolinite surface (N_s). The linear dependence (solid line) is in agreement with the prediction of a simple surface-catalyzed oxalate decomposition reaction mechanism (Eq. (10)).

4.4. The possible effect of microorganism activity on oxalate degradation

A mixture of organic anions, NO_3^- and mineral grains, which may be a possible source for other nutrients, may serve as a culturing medium for microorganisms. The possible presence of bacteria was initially examined by incubating kaolinite and aliquots of solutions taken from the reactor as well from the input and the output bottles onto Luria–Bertani medium for 24 h at 37°C. No growth of microorganisms was found in any of the plates. However, culturing of microbial cells from natural minerals gives unreliable data as only between 0.01% and 10% of microorganisms are culturable by such methods (Banfield et al., 1999).

It is very hard to prove that microorganisms are not affecting a system at low temperature. Even if one sterilizes the system, there is always a possibility that it will be contaminated later on. This potential problem of contamination is more severe in long-term open-system experiments. Even by adding antibiotics to the experiment, one cannot prove that an observed effect is not influenced by microorganism activity as the microorganism may be antibiotic-resistant. On the contrary, if an observed process is halted as antibiotic is added to the system, it is very probable that the process is affected by the presence of microorganisms. Increasing temperature is another possible way to differentiate between a-biotic and biotic processes. We expect that if the oxalate decomposition is catalyzed by the kaolinite surface, the reaction rate will be faster at 50°C than at 25°C. The rate of biodegradation, on the other hand, will depend on the activity of the specific microorganisms at 50°C. As with antibiotics, by increasing temperature one cannot prove that an observed effect is not influenced by microorganism activity, as the microorganism may be resistant at this temperature. However, a process that is halted both by increasing in temperature and by adding antibiotics is most probably controlled by microorganism activity and not by a-biotic processes. Fig. 6 shows the change in the input and output oxalate concentration in a flow-through experiment that was conducted in four stages. The first stage (A) was conducted at 50°C, and no significant oxalate degradation was observed. After more than 40 days at 50°C, the temperature was
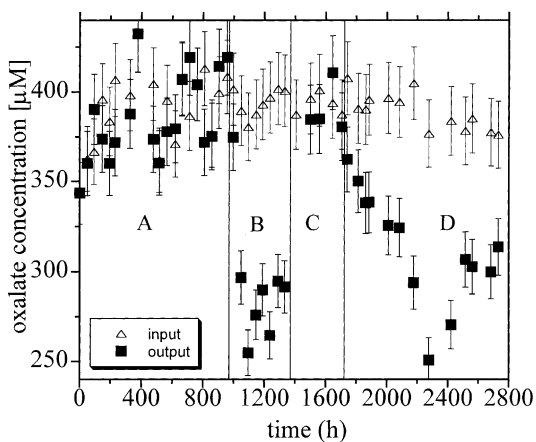
Fig. 6. Changes in oxalate concentration with time in a flow-through experiment that was conducted in four stages: Stage (A) at 50°C; stages (B) and (D) at 25°C; and stage (C) at 25°C with antibiotic.

reduced to 25°C (stage B) and a fast (7×10^{-11} mol s^{-1}) decomposition rate was observed. Adding an antibiotic mixture to the input solution (stage C) halted the oxalate decomposition. The last stage (D) was conducted at 25°C with no antibiotic. As a result, oxalate output concentration decreases until it reaches values similar to those at stage B. The lack of oxalate degradation at 50°C, and in the presence of antibiotics, indicates that there is no significant chemical (a-biotic) decomposition of oxalate in the presence of kaolinite under low-temperature conditions (at pH = 3), and that oxalate decomposition at 25°C is strongly accelerated by the presence of microorganisms. These microorganisms are probably less active at 50°C. The dependence of oxalate-decomposition rate on the kaolinite surface area may indicate that either the microorganisms are attached to the mineral surface or the microorganism population is limited by nutrients that are slowly released from the kaolinite. For example, sample KGa-1 contains low concentrations of potassium ($0.05 \pm 0.01\%$ K_2O) and phosphate ($0.10 \pm 0.01\%$ P_2O_5) (Metz, 2000).

We added the same antibiotic mixture to the adsorption experiments to check whether the microorganisms that enhance the oxalate decomposition in the flow-through experiments are affecting the oxalate concentration during the batch experiments.

Fig. 3 compares the calculated oxalate surface concentration in the presence of antibiotic to that in the absence of antibiotic. In most of the experiments, there is no significant difference between the two data sets (Fig. 3a). The exceptions are experiments that were conducted with very low oxalate concentrations (< 20 μM). Under these conditions, higher surface concentrations are observed in experiments conducted in the absence of antibiotic than in those conducted with antibiotic (Fig. 3b). This antibiotic effect on oxalate adsorption may indicate that either minor amount of the oxalate in the batch experiment is consumed by microorganism activity in the absence of antibiotic or that there is a competition between the oxalate and one of the components of the antibiotic mixture. This competition is significant only when the oxalate concentration is very low. The observation that oxalate concentration ceases to change after the first 30 min of the experiment (Fig. 2) favors the second explanation. The results in Fig. 3 show that the microorganisms that enhance the oxalate decomposition in the flow-through experiments do not significantly influence the changes in oxalate concentration during the batch experiments. Probably, the short duration of the adsorption experiment is not sufficient for a significant growth of the microorganism population. We therefore conclude that our assumption that oxalate decomposition is negligible during the short period of the adsorption experiments is valid, and the concentration of oxalate surface complexes can be determined from the change in oxalate concentration during the batch experiments. The obtained adsorption isotherm (Fig. 3 and Eq. (8)) can be therefore used to study the mechanisms by which oxalate catalyzes the dissolution of kaolinite.

5. Conclusions

The results of the present study show that in long-term flow-through experiments at 25°C and pH 3, oxalate degradation depends on the amount of kaolinite in the system. Although the observations are in agreement with the predictions of a simple surface catalyzed decomposition model, we show that oxalate concentration is controlled by microor-

ganism activity, and not by an a-biotic process. This observation confirms the relative importance of consumption by microorganisms for controlling concentration of low-molecular-weight organic acids in formation water (Lundegard and Kaharaka, 1994). The rate of oxalate consumption by the microorganisms is strongly accelerated by the presence of kaolinite. These microorganisms are less active at 50°C and are affected by the antibiotics mixture used in this study. The mechanisms by which mineral surfaces influence the decomposition of organic acids by microorganisms, and its consequences on the distribution of organic acids should be further examine in future research.

In short (2 h) batch-experiments, on the other hand, oxalate concentration is not influenced by the microorganisms that consumed the oxalate in the flow-through experiments. The fast change in oxalate concentrations during the first 30 min of the batch experiments is best explained by oxalate adsorption on the kaolinite surface. Therefore, these batch experiments can be used to retrieve a reliable estimate of oxalate concentration on the kaolinite surface, and to evaluate possible effect of oxalate surface concentration on kaolinite dissolution rate (Cama and Ganor, in preparation).

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