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EFFECTS OF SORPTION ON THE BIODEGRADATION OF 2-METHYLPYRIDINE IN AQUEOUS SUSPENSIONS OF REFERENCE CLAY MINERALS

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Abstract—The effects of sorption on the bioavailability of 2-methylpyridine (2-MP) were investigated by determining the biodegradation of 2-MP by an *Arthrobacter* sp. in aqueous suspensions of reference clay minerals and a synthetic cation exchange resin. Adsorption of 2-MP on kaolinite, illite, hectorite, montmorillonite, and Dowex® was determined by the batch equilibrium method. In general, adsorption of 2-MP was positively correlated with the cation exchange capacity of the sorbent, suggesting that sorption of 2-MP on clay minerals occurs through a cation exchange reaction via the 2-methylpyridinium ion. The biodegradation of 2-MP was most rapid in the kaolinite suspensions, followed by no clay > illite ≫ Dowex > hectorite/montmorillonite. With the exception of kaolinite, adsorption of 2-MP on clay minerals and Dowex reduced the rate of biodegradation. The degree of attenuation was positively correlated with the fraction of 2-MP sorbed, suggesting that sorbed 2-MP was not directly available for degradation. Desorption was not rate limiting in suspensions containing hectorite, montmorillonite, or Dowex; however, desorption may have become limiting in the kaolinite and illite suspensions. The results of this study clearly indicate that adsorption can directly affect the degradation of 2-MP in complex mineral systems.

Keywords—Biodegradation Bioavailability Sorption 2-Methylpyridine Clay minerals

INTRODUCTION

The ability of microorganisms to degrade organic contaminants (OCs) in terrestrial and aquatic environments is controlled by numerous physical, chemical, and biological factors. Though members of a native (or introduced) microbial community may have the capacity to degrade a given OC, physical and/or chemical constraints may limit degradation. In multiphasic environmental matrices (e.g., soils, sediments, and natural waters), the distribution of OCs in various compartments (e.g., atmospheric, aqueous, micellar, colloidal, and particulate phases) is a function of the thermodynamic constraints on the system and the kinetics of the relevant reactions. Processes that remove OCs from the aqueous phase typically have a marked effect on bioavailability.

While it is commonly accepted that sorption to mineral and organic particulate materials reduces the biodegradation of OCs, presumably by lowering the aqueous-phase concentration of contaminants [1–5], this generalization is not universally true. Several studies have suggested that sorbed substrates may also be degraded [6–9]. Sorption may enhance the biodegradation of toxic compounds by lowering the aqueous-phase concentration, thus decreasing toxicity [10,11]. Biodegradation of sorbed OCs may also be affected by the microbial ecology of a given system since the bioavailability of sorbed OCs can be species specific [6,8].

Alkylpyridines are released into aquatic and terrestrial environments from a number of anthropogenic sources, particularly fossil fuel conversion processes and industrial-scale chemical synthesis. In the waste streams of many oil shale and coal conversion processes, alkylpyridines constitute the major fraction of aromatic *N*-heterocycles (ANHs) present [12,13]. Relative to their homocyclic analogs, these compounds are highly soluble in aqueous solutions. Alkylpyridines are able to migrate through the soil profile [14], which may result in localized groundwater contamination [13,15]. The ANHs are pH-dependent organic cations and thus adsorb to clay minerals and other negatively charged surfaces [16,17]. Adsorption of organic cations to clay minerals has been shown to attenuate their degradation by microorganisms [3,18–20]. Although degradation of alkylpyridines in environmental matrices has been examined [21,22], detailed studies on the bioavailability of adsorbed species are lacking.

The purpose of this investigation was to determine the effects of adsorption on clay minerals on the biodegradation of methylpyridines. Two-methylpyridine (2-MP) was chosen as the model methylpyridine for this study based on the availability of a well-characterized 2-MP degrading bacterium able to grow under pH conditions where sorption of 2-MP to clays is significant. The biodegradation of 2-MP was examined in aqueous suspensions of specimen clay minerals with a range of properties while monitoring sorbed, solution-phase, and total 2-MP concentrations.

MATERIALS AND METHODS

Preparation of clay mineral suspensions

Samples of a poorly crystallized kaolinite from Washington County, Georgia, USA (KGa-2), illite from Silver Hill, Montana, USA (IMt-1), hectorite from San Bernardino County, California, USA (SHCa-1), and a Na-montmorillonite from Crook County, Wyoming, USA (SWy-1) were obtained from the Clay Minerals Society's Source Clays Repository (http://www.agry.purdue.edu/clay/claymin/sourcecl.html). The clays were dispersed by washing with 1 mol/L NaCl, followed by three washes with 50 mmol/L NaCl and three washings with distilled, deionized water. To ensure complete

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dispersion of the kaolinite, the pH of the suspension was raised to 9 with the addition of 1.0 mol/L NaOH. The ≤2-μm size fraction of the clays was collected by sedimentation. To minimize removal of ionic species from solution (i.e., through sorption by clays) required for proper physiological maintenance of the bacteria during the bioavailability experiments, the clay suspensions were washed three times with dilute mineral salts medium (DMSM) prepared from mineral salts medium (3.35 mmol/L KCl, 1.04 mmol/L $MgSO_4$, 0.29 mmol/L K_2HPO_4, 4.70 mmol/L KH_2PO_4, and 1 ml/L trace elements solution [23]) diluted fourfold (to minimize flocculation of clay suspensions). Dowex® 50W-X8 100 to 200 mesh (J.T. Baker Chemical Company, Phillipsburg, NJ, USA), a strongly acidic cation exchange resin, was prepared for use by washing with distilled water and three washes with DMSM.

The cation exchange capacity (CEC) of the clays and Dowex was determined using a mechanical extractor as described by Jaynes and Bigham [24]. The clays were extracted with 1 mol/L NaCl to ensure complete dispersion. The cation-exchange sites were saturated with Ca^{2+} through successive extractions with 1 mol/L $CaCl_2$. The Ca^{2+} was displaced by extraction with 1 mol/L $MgCl_2$. The CEC was determined by analysis of the displaced solution for Ca^{2+} by atomic absorption spectroscopy using a Varian Techtron atomic absorption spectrophotometer model AA6 (Walnut Creek, CA, USA).

Adsorption isotherms

Adsorption isotherms were determined by batch equilibrium in 8-ml-capacity borosilicate glass screw-cap test tubes. Stock clay suspensions were diluted with DMSM to a density of 6 g solids/L and adjusted to pH 6.0 with either 1.0 mol/L HCl or 1.0 mol/L NaOH. Two-methylpyridine is an organic base and can become protonated (pK_a = 5.96), forming 2-methylpyridinium (2-MPH^+). Experiments were conducted at pH 6 to maximize the fraction of 2-MP present as 2-MPH^+ (which is likely to enhance 2-MP sorption) while remaining within the pH range for optimal growth of the *Arthrobacter* sp. to be used in the bioavailability experiments [25]. The suspensions were autoclaved for 20 min at 18 kPa and 121°C. Stock solutions containing 2-MP (98% purity, Aldrich Chemical, Milwaukee, WI, USA) in DMSM were prepared at concentrations from 0 to 600 μmol/L and were filter sterilized through 0.45-μm Nuclepore® (Corning Costar, Cambridge, MA, USA) nylon membrane filters (2-MP was added separately to avoid volatilization losses during autoclaving). When the suspensions had cooled to ambient temperature, 2-ml aliquots of the 2-MP stock solutions were added and the tubes were sealed. All tubes contained 6 ml of suspension with a solids:solution ratio of 4 g/L and from 0 to 200 μmol/L 2-MP. All treatments were performed in triplicate. The suspensions were equilibrated for 24 h at 25°C on a rotary shaker.

After equilibration, subsamples for determination of solution-phase 2-MP were collected by centrifugation (1.65×10^4 g for 10 min). A 0.75-ml aliquot of the supernatant was placed in a 2.0-ml autosampler vial with a screw cap and a Teflon®-lined silicone septum; 0.75 ml of a solution of 50:50 (v:v) high-performance liquid chromatography (HPLC)-grade methanol (Fisher Scientific, Pittsburgh, PA, USA):50 mmol/L ammonium acetate (99% Fisher Scientific) in HPLC-grade water (Fisher Scientific) were added to each. Total 2-MP was determined by extracting 0.75 ml of each suspension with an equal volume of ammonium acetate-saturated methanol in a microcentrifuge tube. The tubes were placed in a sonic bath for 30 min followed by 15 min on an end-to-end shaker. The samples were centrifuged and placed in autosampler vials as described above. The extraction efficiency of this procedure was >90% for all sorbents at 2-MP loadings of 20 to 200 μmol/L and between 65 and 95% with 1 to 20 μmol/L 2-MP, depending on the sorbent. The concentration of 2-MP in the samples was determined by reverse phase HPLC using an Alltech Econosphere C_{18} 220 × 4.6 mm × 5 μm column (Deerfield, IL, USA) with ultraviolet detection at 262 nm. The system was run under isocratic conditions with a mobile phase consisting of 50:50 (v:v) 50 mmol/L ammonium acetate in HPLC-grade water:HPLC-grade methanol at a flow rate of 1 ml/min. The amount of sorbed 2-MP was determined from the difference between the total 2-MP concentration (corrected for extraction efficiency) and the solution-phase 2-MP concentration.

Culture of 2-methylpyridine-degrading bacterium

The organism used in this study was an *Arthrobacter* sp. (American Type Culture Collection 49987) capable of utilizing 2-MP as the primary source of C, N, and energy isolated from subsurface sediments as described previously by O'Loughlin et al. [25]. Cells were cultured in 1 L sterile DMSM with 50 mg yeast extract (added to supply essential growth factors) and 5.0-mmol/L 2-MP. The latter was added aseptically after autoclaving. In late log phase, the cells were collected by centrifugation at 6.38×10^3 *g* at 20°C for 10 min, washed with sterile DMSM, centrifuged, and resuspended to a uniform cell density standardized by measurement of optical density at 660 nm. Cell numbers were determined by colony counts on spread plates following serial dilution.

Biodegradation experiments

Stock clay suspensions were diluted with DMSM to a density of 4 g solids/L suspension and adjusted to pH 6.0 with either 1.0 mol/L HCl or 1.0 mol/L NaOH. Aliquots of suspension (75 ml) were placed in 125-ml Erlenmeyer flasks stoppered with polyurethane foam plugs. Four flasks were prepared for each clay. Flasks without clay were prepared containing 75 ml DMSM. The flasks were autoclaved for 20 min at 18 kPa and 121°C. A stock 2-MP solution containing 9.0 mmol/L was filter sterilized through 0.45-μm Nuclepore nylon membrane filters. When the suspensions had cooled to ambient temperature, 1-ml aliquots of the 2-MP stock solution were added and the suspensions were equilibrated for 24 h at 25°C on a rotary shaker at 180 rpm. The experiments were performed in two series, with series 1 consisting of systems containing no clay, kaolinite, illite, and montmorillonite, and series 2 with no clay, hectorite, and Dowex. All flasks contained 75 ml of suspension with a solids:solution ratio of 4 g/L (except those without clay) and 120 μmol/L 2-MP. Inoculum was added to all flasks, with the exception of the sterile controls, yielding a cell density of 2.9×10^9 cells/ml for series 1 and 3.4×10^9 cells/ml for series 2; series 1 and 2 experiments were run on different dates; therefore, the inocula were prepared from separate stock cultures. A high cell density and low substrate concentration were utilized to minimize changes in the microbial population during the course of the experiments. All treatments were prepared in triplicate. Subsamples were collected from the flasks for analysis of solution phase and total 2-MP prior to the addition of inoculum and at regular intervals thereafter. Solution phase, sorbed, and total 2-MP concentrations were determined as previously described.

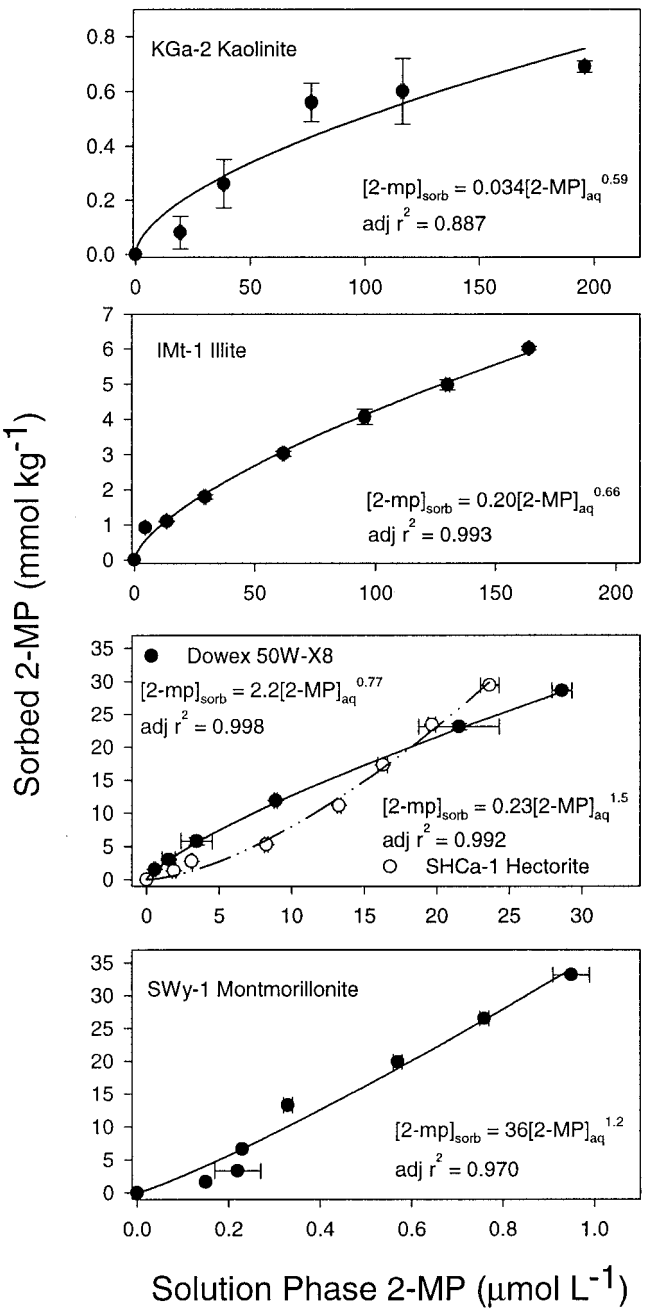

Fig. 1. Adsorption isotherms for 2-methylpyridine on reference clay minerals and Dowex cation exchange resin. Error bars represent 1 SD.

RESULTS AND DISCUSSION

Adsorption of 2-methylpyridine on clay minerals and Dowex

The adsorption isotherms of 2-MP on the reference clays and Dowex were well described by the Freundlich equation (Fig. 1),

$$[\text{2-MP}]_{\text{sorb}} = K[\text{2-MP}]_{\text{aq}}^{n} \quad (1)$$

where $[\text{2-MP}]_{\text{sorb}}$ is the concentration of 2-MP associated with the sorbent, $[\text{2-MP}]_{\text{aq}}$ is the concentration of 2-MP in solution, K is the Freundlich constant, and n indicates the degree of nonlinearity. Though it is not possible to unambiguously determine sorption mechanisms at the molecular level from macroscopic observations (e.g., sorption isotherms), the magnitude of the nonlinearity of the Freundlich isotherm may provide some insight into the sorption process. The isotherms for kaolinite, illite, and Dowex have n values less than 1.0, which is commonly observed in cases where there is a limited number of specific binding sites; as the sorbate concentration increases, sorption of additional molecules becomes more difficult. The Freundlich isotherms for montmorillonite and hectorite had n values greater than 1.0, which may indicate cooperative interactions among sorbed organic species that act to stabilize the adsorbate on the surface and enhance the affinity of the surface for the adsorbed species.

Table 1. Measured and reported cation exchange capacities (CECs) and percent 2-methylpyridine (2-MP) sorbed for reference clay materials and Dowex

Sorbent	Cation exchange capabilities (cmol/kg)		Percent 2-MP sorbed[b]
	Experimental	Reported[a]	
Kaolinite (KGa-2)	3.5	3–15	3.0 ± 0.62
Illite (Imt-1)	17.0	10–40	20.4 ± 1.10
Montmorillonite (Swy-1)	94.5	80–150[c]	99.5 ± 0.01
Hectorite (SHCa-1)	68.0	80–150[c]	86.5 ± 0.29
Dowex® 50W-8X	418.0	490[d]	86.4 ± 0.00

[a] Range of reported CEC values from clay minerals of this type from [34].
[b] Percent of 2-MP sorbed at a total 2-MP concentration of 120 μmol/L.
[c] Range of CEC values for smectite clays.
[d] Reported by manufacturer.

Adsorption of ANHs is generally controlled by a combination of electrostatic, London–van der Waals, and entropic forces. The relative contribution of each to the adsorptive process is dependent on the given adsorbate, adsorbent, and solvent [16,26–29]. The ANHs are organic bases and form cations when protonated. Detailed mechanistic studies of the sorption of pyridine, quinoline, and acridine have indicated that sorption occurs primarily through the protonated species on specimen clay minerals and low organic C soils [17,27,30,31]. Thus, sorption of ANHs on mineral surfaces can be described by the following reactions:

$$\text{ANH} + \text{H}^{+} \leftrightarrow \text{ANHH}^{+} \quad (2)$$

$$\text{ANHH}^{+} + \text{MX} \leftrightarrow \text{M}^{+} + \text{ANHHX} \quad (3)$$

where ANH = aromatic *N*-heterocycle, ANHH^{+} = protonated ANH, M = any inorganic cation, and X^{-} = a unit mole of negative charge on the clay mineral surface.

The sorption mechanism outlined above indicates that the extent of sorption of an aromatic *N*-heterocycle on a given clay mineral is both pH dependent and a function of the abundance of accessible negatively charges sites, which can be estimated by determining the cation exchange capacity of the given clay. The CEC of a clay is a function of both permanent charges (resulting from isomorphic substitution) and pH-dependent charges (resulting from ionization of surface functional groups), which are both dependent on the structural features of the given clay.

The CEC values of the reference clays and Dowex determined in this study are within the range of reported values (Table 1). With the exception of Dowex, the extent of 2-MP sorption was highly correlated to the CEC of the mineral phase. The phase distribution of 2-MP in the clay suspensions ranged from nearly all in solution with kaolinite (3% sorbed at 120

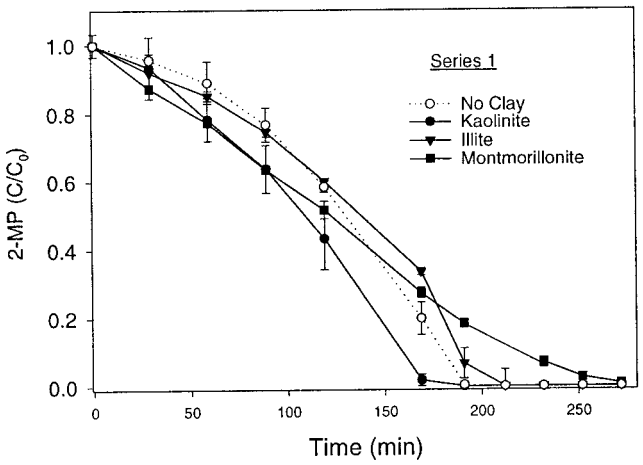

Fig. 2. Biodegradation of 2-methylpyridine (2-MP) in kaolinite, illite, and montmorillonite suspensions (4 g solids/L). Initial 2-MP concentration was 120 μmol/L. Initial cell density was 2.9×10^9 cells/ml. Error bars represent 1 SD.

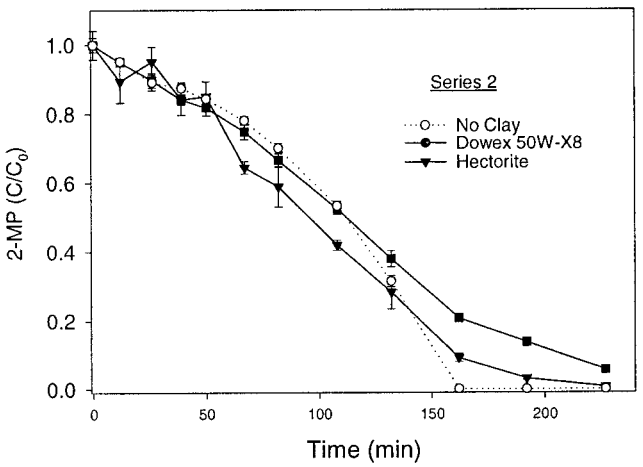

Fig. 3. Biodegradation of 2-methylpyridine (2-MP) in hectorite and Dowex suspensions (4 g solids/L). Initial 2-MP concentration was 120 μmol/L. Initial cell density was 3.4×10^9 cells/ml. Error bars represent 1 SD.

μmol/L 2-MP) to almost completely sorbed with montmorillonite (99+% sorbed). The extent of 2-MP sorption by Dowex was comparatively low relative to its CEC; this may be the result of restricted diffusion of 2-MP into the Dowex copolymer matrix, thus limiting 2-MP sorption to sites on the exterior surface of the beads. Though detailed mechanistic studies of the aqueous-phase adsorption of alkyl-substituted pyridines on clay mineral surfaces are lacking, the data strongly suggest that 2-MP sorption on clays (within the range of 2-MP concentrations examined in this study [10–200 μmol/L]) occurs predominantly as a result of cation exchange by 2-MPH^+.

Biodegradation of 2-methylpyridine

The biodegradation of 2-MP in the test systems is shown in Figures 2 and 3. The degradation of 2-MP was more rapid in systems without clay in series 2 (Fig. 3) than in series 1 (Fig. 2); however, this difference is likely due to the higher initial cell density in series 2 (3.4×10^9 cells/ml) relative to series 1 (2.9×10^9 cells/ml). Indeed, the times required for complete degradation (191 min for series 1 and 162 min for series 2) are exactly proportional to the initial cell densities. The overall patterns of the degradation curves in each series were similar. During the initial 90 min, there was a slight enhancement of 2-MP degradation in systems containing sorbents relative to the control. After 90 min, the degradation curves indicate a change in the relative effects of the sorbents. In series 1, 2-MP was degraded most rapidly in the system containing kaolinite, with <2% remaining after 169 min, as compared with 20% remaining in the system without clay. At 191 min, <1 and 7% remained in the no-clay and illite systems, respectively. The degradation of 2-MP was most attenuated with montmorillonite; <1% of the initial 2-MP remained after 272 min. In series 2, 1% of 2-MP remained in flasks without clay at 162 min, while 12 and 25% remained in the systems containing Dowex and hectorite, respectively. Even after 227 min, 7% of the initial 2-MP remained in the hectorite suspensions.

The complexity of the data limits the applicability of commonly utilized biodegradation kinetics models (e.g., first order and Monod) to describe 2-MP degradation in these experiments. However, for the purpose of comparison among treatments, degradation rates were estimated by linear regression of data from the most linear portion of the degradation curves (90–190 min for series 1 and 80–160 min for series 2). The degradation rates for the controls from each series were proportional to the initial cell densities (Table 2), which again suggests that the slower degradation of 2-MP in the controls in series 1 is a result of the smaller microbial population. With the exception of kaolinite, the degradation rates in the clay

Table 2. Degradation rates for 2-methylpyridine (2-MP) in controls and with sorbents

Sorbent	Rate[a] (μmol/L/min)	r^2	Relative rate[b] (μmol/L/min)
Series 1			
No clay	−0.894 ± 0.038[c]	0.998	0.000
Kaolinite (KGa-2)	−0.925 ± 0.065	0.998	−0.031
Illite (Imt-1)	−0.848 ± 0.098	0.996	0.046
Montmorillonite (Swy-1)	−0.545 ± 0.016	0.998	0.349
Series 2			
No clay	−1.099 ± 0.083	0.994	0.000
Hectorite (SHCa-1)	−0.702 ± 0.001	0.998	0.337
Dowex 50W-8X	−0.772 ± 0.013	0.999	0.278

[a] Calculated from linear portion of degradation curves (Fig. 2, 90–190 min; Fig. 3, 80–160 min).
[b] Rates relative to systems without clay (series 2 rates were normalized to rate for the system without clay in series 1).
[c] Rate ± SE.

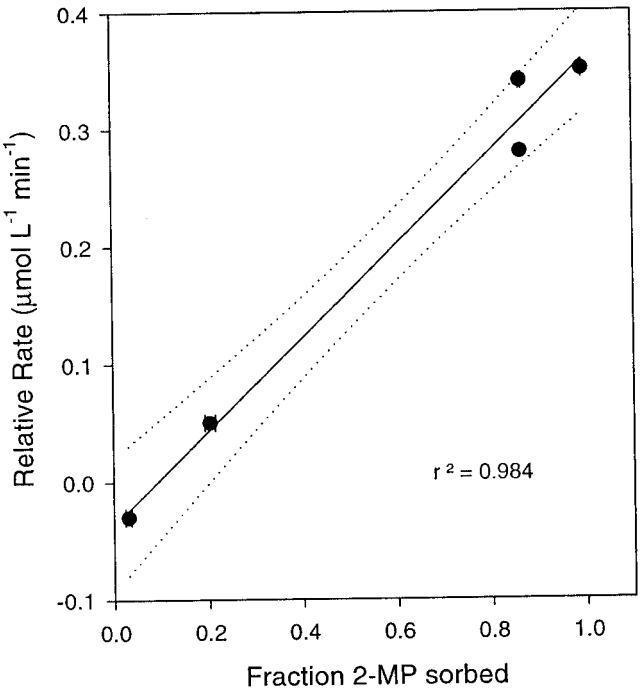

Fig. 4. Correlation between relative rate of 2-methylpyridine degradation (2-MP) and 2-MP sorption on reference clay minerals and Dowex cation exchange resin. Error bars represent 1 SD. Dashed lines indicate 95% confidence intervals.

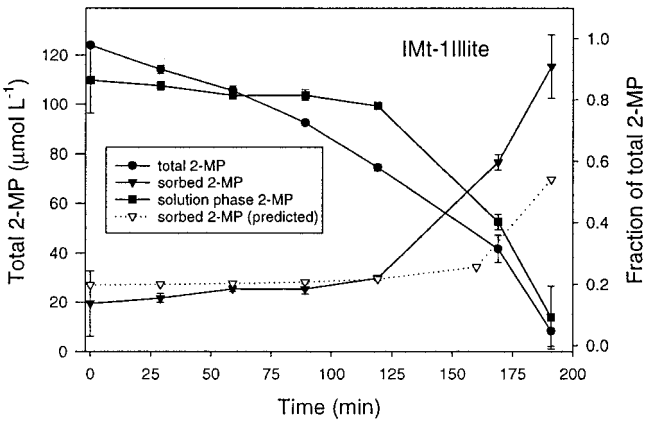

Fig. 5. Distribution of 2-methylpyridine (2-MP) during biodegradation in an aqueous suspension of illite (4 g solids/L). Initial 2-MP concentration was 120 μmol/L. Initial cell density was 2.9×10^9 cells/ml. Sorbed 2-MP concentrations were corrected for extraction efficiency. Sorbed and solution-phase 2-MP are expressed as fractions of the remaining 2-MP. Values for the predicted fraction of sorbed 2-MP were calculated from the fitted sorption isotherm curve, $[2\text{-MP}]_{sorb} = 0.20[2\text{-MP}]_{aq}^{0.66}$. Error bars represent 1 SD.

suspensions and Dowex were attenuated relative to the control. Overall, the degradation rate was highest in the kaolinite suspensions, followed by no clay > illite ≫ Dowex > hectorite/montmorillonite. There was a strong correlation between the normalized degradation rates and the extent of 2-MP sorption (Fig. 4), suggesting that sorption limited degradation.

If sorption were the only factor affecting 2-MP degradation in the clay suspensions, then the degradation of 2-MP in kaolinite suspensions (where only 3% of the 2-MP is sorbed) should have been similar to the controls. Instead, 2-MP degradation was enhanced in the presence of kaolinite. This observation is not unique. Weber and Coble [18] reported enhanced degradation of diquat in the presence of kaolinite (while montmorillonite inhibited diquat degradation). The association of microbes with surfaces has been shown to enhance growth in specific systems [32]. Since the *Arthrobacter* sp. used in this study was isolated from subsurface materials, its physiology may be optimized when associated with surfaces, as suggested by the enhanced degradation of 2-hydroxypyridine by *Arthrobacter crystallopoietes* in the presence of clay minerals under growth-limiting conditions reported by Hwang and Tate [33]. The observed enhancement of 2-MP biodegradation in the kaolinite suspensions may have been due to unique structural properties of kaolinite or may have occurred with all the sorbents had the effect not been overwhelmed by the effects of sorption on bioavailability in those systems.

Given the high cell density relative to the substrate concentration, it is reasonable to assume that degradation occurred with a static microbial population. Under these conditions, the degradation rate should be a function of the concentration of the substrate. Assuming that the clay itself does not affect the physiological response of the bacteria, the degradation rates should be similar for all treatments if the total 2-MP pool (sorbed and solution phase) is available for degradation. Clearly, this was not the case in this study. The general decrease in degradation rate with increasing 2-MP sorption (Fig. 4) indicates that adsorbed 2-MP was less available for bacterial transformation than solution-phase 2-MP. In general, degradation rates appeared to be a function of the solution-phase concentrations, indicating that sorbed 2-MP must desorb to become available.

Our results are consistent with the paradigm proposed by Ogram et al. [1] to describe the effects of sorption on the biodegradation of 2,4-D in soils, namely, that in the absence of microbial limitations, biodegradation is limited by the solution-phase concentration. This model has been used to describe the effects of sorption on biodegradation in a number of systems, including toluene in soils [2], benzylamine with montmorillonite [20], and quinoline with hectorite and montmorillonite [3]. There have been several studies that suggest that sorbed substrates may be degraded by bacteria attached to sorbents [6,7,9]. However, it is not clear from the data whether the organisms were directly degrading sorbed material (i.e., direct uptake of sorbed substrates by attached bacteria without prior desorption into the aqueous phase) or instead were degrading substrate that desorbed into the thin film (<200 μm) of stagnant water on the surface of the sorbent (unlike unattached bacteria, which must wait until the desorbed substrate has diffused into the bulk solution).

Distribution of 2-methylpyridine during biodegradation

The distribution of 2-MP between sorbed and solution phases was monitored throughout the course of the biodegradation experiments. For kaolinite and illite (sorbents with relatively low affinities for 2-MP), little 2-MP is sorbed; thus, the majority of 2-MP is in solution at equilibrium. During the degradation of 2-MP in illite suspensions (Fig. 5), solution-phase 2-MP was the dominant form. The system appeared to remain at equilibrium with respect to the distribution of 2-MP between sorbed and solution phases as shown by the agreement between the measured fraction of sorbed 2-MP and the sorbed fraction predicted by the sorption isotherm data. However, after ~40% of the 2-MP was degraded, the system no longer remained at equilibrium with respect to the distribution of 2-MP as dem-

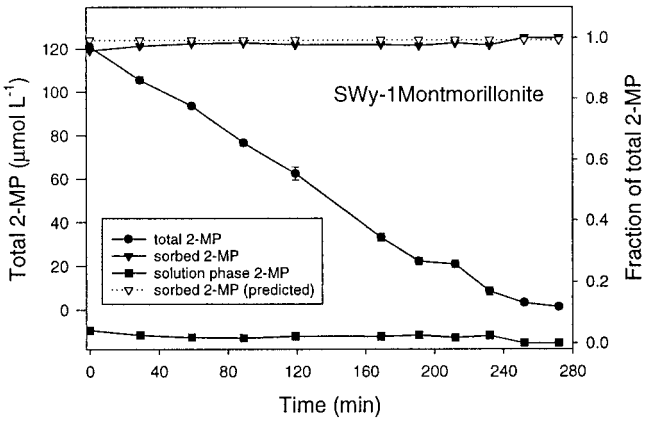

Fig. 6. Distribution of 2-methylpyridine (2-mp) during biodegradation in an aqueous suspension of montmorillonite (4 g solids/L). Initial 2-MP concentration was 120 μmol/L. Initial cell density was 2.9×10^9 cells/ml. Sorbed 2-MP concentrations were corrected for extraction efficiency. Sorbed and solution-phase 2-MP are expressed as fractions of the remaining 2-MP. Values for the predicted fraction of sorbed 2-MP were calculated from the fitted sorption isotherm curve, $[2\text{-MP}]_{sorb} = 36[2\text{-MP}]_{aq}^{1.2}$. Error bars represent 1 SD.

onstrated by the greater extent of 2-MP sorption relative to the predicted levels. Under these conditions, 2-MP was degraded in solution faster than it was desorbed. Similar results were observed in the kaolinite suspensions (data not shown). With hectorite, montmorillonite, and Dowex (which have comparatively high affinities for 2-MP), most of the 2-MP is sorbed under equilibrium conditions. The distribution of 2-MP in the montmorillonite suspensions (Fig. 6) as well as for hectorite and Dowex (data not shown) remained unchanged throughout the 2-MP degradation experiments. The majority of the 2-MP was sorbed; however, unlike in the kaolinite and illite suspensions, sorption did not appear to become limiting; measured sorbed 2-MP did not exceed levels predicted from sorption isotherm data.

CONCLUSIONS

In general, adsorption of 2-MP was positively correlated with the CEC of the adsorbent, suggesting that adsorption of 2-MP occurred through a cation exchange reaction via the 2-methylpyridinium ion. Degradation of 2-MP in clay suspensions appeared to be controlled by the concentration of the substrate in solution phase, suggesting that sorbed 2-MP was not directly available. The degree of attenuation of biodegradation was consistent with the degree of 2-MP adsorption on the surface of the given solid phase. Depending on the relative rates of microbial degradation and desorption of the substrate from the surface, the degradation rate may be limited by desorption [3] or microbial uptake [20]. It appeared that desorption was not rate limiting in suspensions containing hectorite, montmorillonite, or Dowex; however, desorption may have become limiting in the kaolinite and illite suspensions.

The results presented in this study provide significant insight into the bioavailability of alkylpyridines in aqueous clay mineral suspensions. However, a single 2-MP-degrading strain was used in a well-defined and rigorously controlled system. Care must be taken in extrapolating these results to conditions commonly found in terrestrial and aquatic environments, which typically have mixed microbial populations, lower total substrate concentrations, and heterogeneous soil-sediment composition. Nevertheless, the results of this study indicate that adsorption processes can directly effect the degradation of 2-MP in complex mineral systems. Clearly, attention must be paid to these phenomena when assessing the fate of strongly sorbing organic solutes in soils, aquifers, and other natural porous media.

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