Changes of the density of charge on mineral soil components by adsorption of some metabolites of hydrocarbons

Abstract The adsorption on clay minerals and sesquioxides of some polar degradation products of naphthalene and alkylated benzenes was investigated by $^{14}$C-tracer experiments. Surface charge density of the solids was measured by titration with sodium polyethylene sulfonate and polydiallyl-dimethyl-ammonium chloride at pH-range 4—7. Adsorption of organic anions reduced the positive charge on oxidic surfaces and increased the density of negative charge on clay minerals, respectively. The increase of the density of charge on clay minerals indicated an effective bonding mechanism. Changes of the density of charge were due to the adsorption of anions. The method is suitable for screening the interaction between polar metabolites of hydrocarbons and mineral soil components.

Key words Adsorption — clay minerals — hydrocarbons — particle charge — sesquioxides

Introduction

In recent years a large number of hydrocarbon-contaminated sites has been discovered. As a consequence, microbial clean-up technologies have been developed. It has been shown, however, that the restoration of sites contaminated with lubricating oils or other complex mixtures is very complicated [1]. The biodegradation of the substances is often limited to secondary formation of alcohols and acids. There is little information about the interaction of polar substances with soils that have a low carbon content, although the importance of mineral soil components as adsorbents of organic chemicals is now generally accepted [2, 3]. The aim of the paper is to describe changes of surface characteristics of mineral adsorbents especially of the density of charge by adsorption of polar aromatic degradation products.

Methods and materials

Model components of soils

The major constituents of soils are sesquioxides and clay minerals. Iron oxide (goethite) was synthesized by a method described by Gerth [4] and manganese oxide (manganite) was prepared by a method described by McKenzie [5]. The clay mineral montmorillonite was obtained from Wyoming, USA, while kaolinite was obtained from Ward Corp., USA. Organic substances were destroyed by a pretreatment of the clay minerals with H$_2$O$_2$. The surfaces were loaded with calcium chloride and adjusted to pH 7.

All minerals were characterized by x-ray-diffractionometry. The components were stored as a suspension in the dark at 5°C. Table 1 shows some important characteristics of the components. The measurement of the specific surface area was done by N$_2$-
Table 1 Characteristics of the soil components

<table>
<thead>
<tr>
<th></th>
<th>Particle size (μm)</th>
<th>Spec. surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manganite</td>
<td>0.10 × 10</td>
<td>13.9</td>
</tr>
<tr>
<td>Goethite</td>
<td>0.03 × 0.80</td>
<td>62.7</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>0.20—2.00</td>
<td>67.2</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>1.00—10.0</td>
<td>7.9</td>
</tr>
</tbody>
</table>

adsorption and calculation of the BET-Isotherm. The particle sizes were measured by scanning and transmission electron microscopy (SEM, TEM).

Metabolites of hydrocarbons

2-hydroxybenzoic acid (salicylic acid) and 1,2-dihydroxybenzene (catechol) were used as catabolite products of naphthalene, benzoic and 4-methylbenzoic acid were used as degradation products of alkylated aromatic substances, which were important constituents of lubricating oils. The biodegradation of naphthalene by bacteria has been described [6], and aromatic acids have been found in groundwater that has passed a site contaminated by alkylated benzenes [7]. The substances were obtained from Sigma Chemie, FRG.

Experiments with 14C-tracers

Experiments with radioactive chemicals were performed to receive ensured information about the distribution of the metabolites in the suspension. The experiments were carried out at different pH values. In the same way the concentration of calcium chloride was varied between 1.3 and 3.2 μmole/l. The concentration of the metabolites was 9 μmole/l and that of the solids was 300 mg/l. The vials which were used during this assay had a volume of 6 ml and were kept under constant shaking for 4 days at 21°C. After this time, the solid phase was separated by centrifugation. Measurement of radioactivity was done by β-scintillation counting. The comparison of the radioactivity in the aqueous phase with a solid free variant was used to describe the association of organic compounds with the mineral soil components. All experiments were done in triplicate.

Measurement of the charge density

The density of charge of the soil components was measured by a “particle charge detector” constructed by Miitek, FRG. The suspension was filled into a cylindrical testing apparatus and a large fraction of the solids was adsorbed on its wall. As a function of pH and characteristics of the soil constituents these solids are charged except at the point of zero charge. Charge equalization is achieved by the sorption of counterions. During the measurement this equilibrium is disturbed by a laminar flow generated by a piston stroke. The spatial shift of the counterions generates an electrical potential, which can be recorded and counted by detectors at the ends of the testing arrangement. The suspension was titrated with a polyelectrolyte and in this way the charge of the solids was compensated. When the counterionic space charge cloud disappears and the value of the electrical potential drops to zero, the density of charge σ can be calculated as follows:

\[ \sigma = \frac{V \cdot c(PE) \cdot F}{m \cdot A/m}, \]  

where \( V \) is the volume of the titrating solution, \( c(PE) \) is the concentration of the polyelectrolyte, \( F \) is the Faraday constant (9,64845 × 10⁴ C/mole), \( m \) is the mass of the particles, and \( A/m \) is the specific surface area of the solids.

Preliminary tests have shown a decrease of titration speed at the end of the measurement, and much time is needed to obtain a result. Sporadically, the reaction between the polyelectrolyte and the surfaces was not finished, and a second titration step was necessary. Because of these disadvantages the samples were not titrated in this way. Instead, the solids were treated with an excess of polyelectrolyte. The mass of the non reacting polyelectrolyte was determined by back-titration with the opposite kind of polyelectrolyte. In Eq. (1) the term \( V \cdot c(PE) \) has to be substituted as follows:

\[ V \cdot c(PE) = V_0 \cdot c(PE_0) - V_T \cdot c(PE_T), \]  

where \( V_0 \) is the volume of the polyelectrolyte, which was used in excess, and \( c(PE_0) \) is its concentration. \( V_T \) is the volume of the polyelectrolyte solution which was used for back-titration, and \( c(PE_T) \) is its concentration. In relation to the sign of the charge of the soil compounds counterionic and isoionic polyelectrolytes were used. The sign of \( V \cdot c(PE) \) is identical with the sign of the charge at the surface if \( PE_0 \) is the anionic and \( PE_T \) the cationic polyelectrolyte. Sodium polyethane sulfonate was used as anionic polyelectrolyte and polydiallyl-dimethyl-ammonium chloride was used as a cationic one.

The experiments were carried out as follows: 3 mg of a mineral soil component were transferred with a pipette as a suspension into 20-ml glass vials. 5 μmole of polyelectrolyte, 0.3 μmole of calcium chloride and different amounts of hydrochloric acid (HCl) and sodium hydroxide (NaOH), respectively, were pipetted into the vials, which were filled up to 10 ml with demineralized water. The vials were shaken for 1 week in the dark at room temperature. All experiments were done in triplicate.