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

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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 polyethene 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_2O_2. The surfaces were loaded with calcium chloride and adjusted to pH 7.

All minerals were characterized by x-ray-diffractometry. 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

	Particle size (μm)	Spec. surface area (m²/g)
Manganite	0.10 × 10	13.9
Goethite	0.03 × 0.80	62.7
Montmorillonite	0.20— 2.00	67.2
Kaolinite	1.00— 10.0	7.9

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 Mütek, 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:

$$\sigma = \frac{V \cdot c(PE) \cdot F}{m \cdot A/m} \, , \tag{1}$$

where V is the volume of the titrating solution, $c(PE)$ is the concentration of the polyelectrolyte, F is the Faraday constant $(9,64845 \cdot 10^4 \text{ C/mole})$, 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:

$$V \cdot c(PE) = V_0 \cdot c(PE_0) - V_T \cdot c(PE_T) \, , \tag{2}$$

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_I 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.

pH and metabolites

An interaction between the metabolites and the polyelectrolytes was investigated by titrating solid free controls at pH 5 and 8, respectively. Results that differ significantly from the values obtained from back-titrating the counterionic polyelectrolyte could be observed in the alkaline controls. Therefore, the following experiments were carried out at lower pH values. Some data were obtained from alkaline controls that did not contain any metabolites.

The concentration of hydronium ions was adjusted to pH values between 3 and 7. The concentration of the metabolites was 500 µmole/l. The concentration of 4-methylbenzoic acid was 250 µmole because of the limited solubility. The polar organic chemicals existed as anions with the exception of 1,2-dihydroxybenzene.

Calcium chloride assay

In the presence of high concentrations of calcium chloride the spatial extent of the electric field around the soil colloids was reduced significantly. The recording and counting of the electrical potential was difficult and was partly not possible. Beyond this, the experimental results dependend on the concentration of calcium chloride. The reason for this might be an interaction between calcium chloride and the polyelectrolytes or a modification of the solid surfaces.

These preliminary studies have shown that the concentration of calcium chloride should not significantly exceed 30 µmole/l, if a solid concentration of 300 mg/l is chosen. The tests were carried out at this concentration and were compared with experiments without calcium chloride to investigate the effects of this electrolyte.

Results

Tracer assay

Figure 1 shows the adsorbed mass (m_{ad}) related to the total mass (m_t) of the metabolites in the tests. The results were derived from the comparison of the radioactivity of the supernatant and the radioactivity of the solid free control. Sorption of less than 3% of the total mass was not significant.

As a unitary result, it was found that the sorbed mass increased with decreasing pH values. Protonation of the surfaces of the solids with an increased affinity to anions might be the reason for this, rather than a hydrophobic effect. The pH-values were some orders above the pk_s-values of the acids. There was no interaction between any soil component and the substance with the highest octanol-water-partition coefficient P_{ow}, which is 2.27 for 4-methylbenzoic acid. This result emphasizes the polar properties of the mineral soil particles in the suspension.
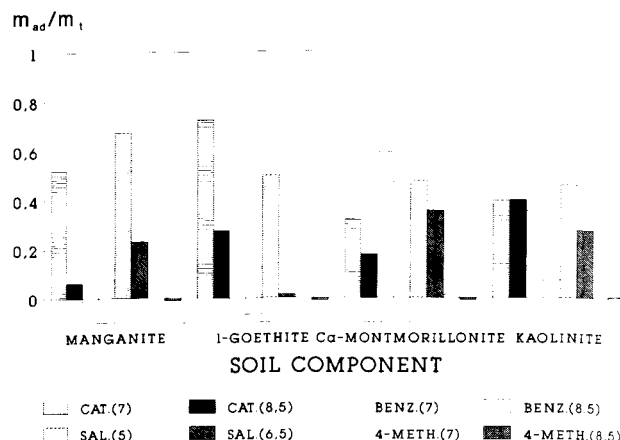

Fig. 1 Sorption of the metabolites on the solids at different pH values, ^{14}C-tracer assay

There was no difference in partitioning of the metabolites at different concentrations of calcium chloride (1.3 and 3.2 µmole/l, respectively) that lies above the range of variations of these measurements.

The interactions between goethite and benzoic acid were unexpected and a plausible interpretation cannot be given here.

Density of charge

pH value

The results of the measurements carried out with an excess of cationic electrolyte and with calcium chloride are shown in Figs. 2—3. An increase of the hydronium ions concentration in the aqueous phase is coupled with an increase of the positive charge of the particles. This can be derived from the slope of the regression line. This result was expected because of the interaction of the hydronium ions with the surfaces of the soil components. The value of the slope is higher for sesquioxides in comparison with clay minerals. The surface of montmorillonite is negatively charged because of the permanent charge.

Interactions with the metabolites

As demonstrated in Fig. 2, organic substances interact with the positively charged surface of manganite. The positive charges were reduced in the order 4-methylbenzoic acid, 2-hydroxybenzoic acid, 1,2-dihydroxybenzene. If goethite is used as an adsorbing substance, only the reduction of the positive charge by sorption of 1,2-dihydroxibenzene is significant. Beyond that, both oxides react with the phenolic compound 1,2-dihydroxibenzene, forming green-colored complexes.
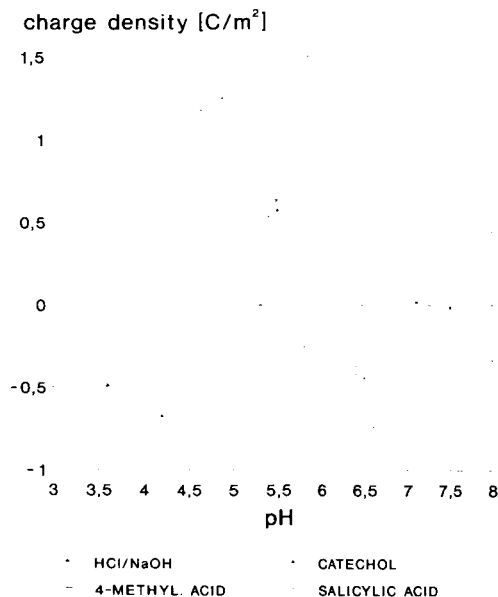
charge density [C/m²]

Fig. 2 Changes of the charge density σ on manganite at different pH values in the presence of metabolites
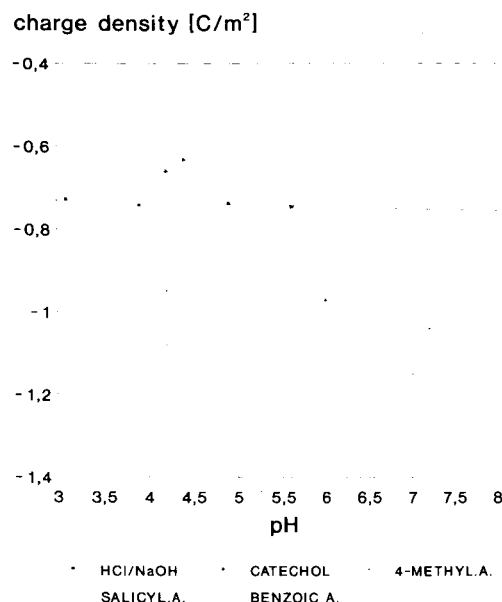
charge density [C/m²]

Fig. 3 Changes of the charge density σ of on montmorillonite at different pH values in the presence of metabolites

The density of charge is nearly constant over the whole range of pH if clay minerals are tested (Fig. 3). The negative charges increase in the order 1,2-dihydroxy-benzene, 4-methylbenzoic acid, benzoic acid, 2-hydroxy-benzoic acid. The change of the charge density strongly depends on the pH if 1,2-dihydroxibenzene is the metabolite.

No change of the density of charge was seen in the experiments carried out with the organic anions and kaolinite as adsorbent. All experiments performed at an excess of anionic polyelectrolyte show high values of the mean error, and therefore changes in the density of charge were not significant.

Calcium chloride assay

The presence of calcium chloride at the concentration of 30 μmole/l reduced the order of magnitude of the mean error of the measuring points around the regression line of the hydronium ions adsorption by HCl and NaOH, respectively. At least the variance of the values was the result of the instability of the system during pH measurement and when no additional electrolyte was present. As a rule, more than 10 minutes were required to get values that could be regarded as reliable.

Discussion

Changes of the density of charge observed during the adsorption of some metabolites of hydrocarbons on mineral soil components were compared with the results derived from partitioning experiments with radiochemicals. Some hints at the interaction between 1,2-dihydroxybenzene and related compounds, respectively, with iron ions [8] or Al-OH groups [9] were found in the literature. Sigg and Stumm [10] emphasized the reactivity between metal hydroxides and those chemicals forming ring-shaped surface complexes like 2-hydroxybenzoic acid.

The adsorption of organic anions reduces the positive charge of the oxidic surfaces of manganite and goethite and increases the density of negative charge of montmorillonite, respectively. While the neutralization of positive charges on protonated surfaces by adsorbing anions seems to be plausible because of electrostatic reasons, changes in the density of charge indicate an effective bonding mechanism if — as in the case of montmorillonite — Coulomb forces were surmounted.

Changes of the density of charge were due to the adsorption of anions. The measurements of the density of charge were semiquantitative, because the interaction between metabolite and polyelectrolyte has to be taken into account. The developed method could be useful to obtain some quick information about the interaction between organic substances and soil components without using radiotracer tests, which are more sophisticated when contaminated sites have to be investigated to develop clean up strategies.

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