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Influence of Soil Organic Matter Composition on the Partition of Organic Compounds

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■ The sorption at room temperature of benzene and carbon tetrachloride from water on three high-organic-content soils (muck, peat, and extracted peat) and on cellulose was determined in order to evaluate the effect of sorbent polarity on the solute partition coefficients. The isotherms are highly linear for both solutes on all the organic matter samples, which is consistent with a partition model. For both solutes, the extracted peat shows the greatest sorption capacity while the cellulose shows the lowest capacity; the difference correlates with the polar-to-nonpolar group ratio $[(O + N)/C]$ of the sorbent samples. The relative increase of solute partition coefficient (K_{om}) with a decrease of sample polar content is similar for both solutes, and the limiting sorption capacity on a given organic matter sample is comparable between the solutes. This observation suggests that one can estimate the polarity effect of a sample of soil organic matter (SOM) on K_{om} of various nonpolar solutes by determining the partition coefficient of single nonpolar solute when compositional analysis of the SOM is not available. The observed dependence of K_{om} on sample polarity is used to account for the variation of K_{om} values of individual compounds on different soils that results from change in the polar group content of SOM. On the assumption that the carbon content of SOM in "ordinary soils" is 53-63%, the calculated variation of K_{om} is a factor of ~ 3 . This value is in agreement with the limit of variation of most K_{om} data with soils of relatively high SOM contents.

Introduction

A series of earlier studies on the sorption of organic compounds by soil in aqueous systems substantiate the idea that soil organic matter (SOM) functions primarily as a partition medium in the uptake of these compounds from water (1-11). By contrast, the mineral matter of the soil is identified as an adsorbent in uptake of organic compounds. This accounts for the strong uptake of organic compounds by dry soils and minerals and for other isotherm characteristics (4-6, 12, 13). The often observed dependence on SOM content of the organic compound uptake by soil in aqueous systems is the consequence of the suppression of mineral adsorption that results from powerful polar interactions of water with mineral surfaces. Supporting evidence for the partition uptake by SOM consists of linear sorption isotherms of organic solutes and vapors to high relative concentrations (1-4), low heat of solute sorption (1, 10), lack of apparent competitive effects in the uptake of binary solutes (3, 4), compatibility of the sorption data with the Flory-Huggins theory for solute solubility in organic (amorphous) polymers (3, 11), and the small surface areas of SOM as determined by the standard BET (N_2) method (7).

Although the partition model with SOM has successfully explained a wide variety of data on organic compound sorption by soil from water (6-12, 14), and although the normalization of solute sorption coefficients on the basis of SOM (K_{om}) or soil organic carbon (K_{oc}) has greatly reduced the divergence of the results (15, 16), significant differences in K_{om} (or K_{oc}) values of various compounds are often observed between soil samples of different origins

(15-17). These differences can result from various intrinsic properties of the SOM and external factors (including different equilibration procedures and analytical inaccuracies in determining the amounts of sorption). As a rule, data derived from samples of low SOM contents tend to be more variable; this variability is due in good part to the increased difficulty in quantitation of trace organic contents in the sample and to the small uptake by the sample, which results in small concentration differences between pre- and postequilibrium values.

From the standpoint of partition interactions of solutes with SOM, certain differences are expected to occur in the partition efficiency of a given compound with SOMs of different geographic sources because the compositional differences would affect the solute solubility. The effect of organic matter composition on organic solute partition was illustrated earlier by Chiou et al. (18, 19) and Garbarini and Lion (20) in the study of the extent of solute (partition) interactions with humic and fulvic acids extracted from soils and river waters, in which the solute partition efficiency decreased with increasing polar group content of the humic and fulvic acids. While a similar effect is expected for the indigenous organic matter in soil, no quantitative data are available in this respect, and consequently, the extent to which this effect contributes to the observed variability of the K_{om} values of given solutes with different soils is not known. For ordinary soil samples, which are relatively low in SOM content, attempts to investigate the compositional effect of SOM are usually hindered by (i) the need of sufficient quantities of SOM to be removed from soils for reliable compositional analysis and (ii) the possible compositional change of SOM associated with the use of chemical agents to extract organic matter from soil. It is therefore advantageous that studies of the dependence of the sorption coefficient on SOM composition be carried out on intact natural soil/sediment samples of high organic content to render accurate determinations of sorption coefficients and SOM composition.

In this study, we initiated investigations of the effect of SOM composition on sorption efficiency by selecting cellulose and a series of high-organic-content soils (muck, peat, and extracted peat) as model natural organic matter. The inclusion of extracted peat (in which the polar group content is reduced by solvent extraction) and cellulose along with peat and muck extends the range of the organic composition (i.e., differences in carbon and oxygen contents) that should cover the likely range of soil organic composition of normal soils. In view of the abundance of cellulose in plants and its wide industrial applications as the raw material for paper, clothing, and filter, findings on the sorption characteristics of cellulose would provide technical data for assessing the extent of environmental organic compound uptake by plant litter and disposed paper and clothing materials. Benzene and carbon tetrachloride, two widely spread organic contaminants, were selected as test solutes. These two solutes have well-defined water solubilities, which facilitate a close examination of their sorption (partition) effects in relation to their solubilities.

Table I. Surface Areas and Percent Elemental Contents of Organic Matter Samples on a Moisture-Free, Ash-Free Basis

material	surface area, m ² /g	C	H	O	N	S	ash
extracted peat	ND ^a	64.0	4.40	28.9	2.36	0.27	15.0
peat	1.5	57.1	4.49	33.9	3.60	0.65	13.6
muck	0.8	53.1	4.90	37.5	3.77	0.48	18.5
cellulose	2.3	44.4	6.20	49.4	0.0	0.0	0.0

^a ND, not determined.

Experimental Section

The carbon tetrachloride and benzene were 99+% spectrophotometric grade from Aldrich Chemical Co. Cellulose was obtained from Aldrich Chemical Co. as a 20- μ m powder. The peat sample is the reference sample of the International Humic Substances Society collected from Everglades, FL. The Houghton muck soil was obtained from the Michigan State University Muck Research Farm, Lainsburg, MI.

The extracted peat was obtained by extracting the peat with 0.1 M NaOH solution. Fifty grams of peat was shaken with 150 mL of 0.1 M NaOH on a mechanical shaker for 24 h. The peat slurry was centrifuged for 1 h at 10400g and the supernatant was decanted. This extraction procedure was repeated 50 times. The extracted peat was finally washed three times with deionized water and freeze-dried.

Elemental analyses of the peat, muck, and extracted peat were performed by Huffman Laboratories, Golden, CO. A detailed description of the analytical method is presented by Huffman and Stuber (21). The BET surface areas were determined by nitrogen adsorption at liquid nitrogen temperature, using a Quantasorb surface area analyzer and the triple-point method. The composition of cellulose was taken from the formula (C₆H₁₀O₅)_n. Results of these analyses are shown in Table I.

The ratios of organic matter sample to water in sorption experiments were selected to give more than 50% of the solute uptake by the sample. Samples were prepared in duplicate. The samples were weighed into 25-mL screw-capped Corex centrifuge tubes, filled to minimal headspace with water containing 0.005 M CaCl₂, and weighed to determine the water volume. Known volumes of neat benzene or carbon tetrachloride were injected into the tubes by precision microsyringe. The tubes were immediately sealed with a cap having an aluminum liner backed by Teflon. The samples were mixed for 3–5 days on a rotary mixer at room temperature (24 \pm 1 $^{\circ}$ C).

After equilibration, the tubes were centrifuged for 1 h at 2990g to settle the solids. A 2-mL aliquot of the supernatant was removed and extracted with 2 mL of hexane by shaking for 5 min on a mechanical shaker. The solute concentration was analyzed on a gas chromatograph equipped with a 25-m, 0.32-mm-diameter capillary column coated with cross-linked 5% phenyl methyl silicone (0.52- μ m thickness). A flame ionization detector was used.

The remaining aqueous portion in the sample tube was removed by aspiration. The tubes were reweighed to determine the residual water content, and 20 mL of 1:4 acetone/hexane solvent mixture was added to extract the solute. The extraction was performed on a rotating mixer for 24–48 h, and the extract was analyzed for solute concentration by gas chromatography as described. The solute uptake by the organic matter was corrected for the amount of residual water. Except for cellulose, this method was more accurate than measurement by the difference of the

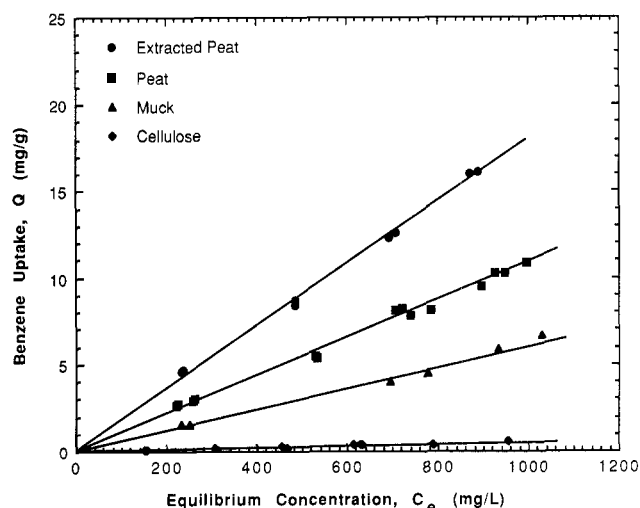


Figure 1. Uptake of benzene from water by selected organic matter samples.

original amount added and the amount in solution at equilibrium.

The determined concentration of solute in the solid organic matter sample (Q) at equilibrium and the corresponding concentration in water (C_e) were used to establish sorption isotherms. All isotherm data except for those with cellulose were based on Q derived by direct extraction from the solid. Mass balances for these points were all better than 90% with most greater than 95%. Due to the large sample size of cellulose used (5.0 g) and its tendency to swell, direct extraction of solutes from cellulose samples was difficult. The uptake data with cellulose were obtained by the difference of the original amount added and the amount in solution at equilibrium.

Blank experiments were run with peat and muck samples (1 g) and 0.005 M CaCl₂ solution (20 mL) without test solutes to determine the level of "dissolved organic matter" (DOM) in aqueous phase of the sorption experiment that results from the solubility and dispersion of the sorbent sample. This sample-to-water ratio corresponded to the upper limit of DOM in all sorption experiments. The determined dissolved organic carbon (DOC) level was used to evaluate the potential impact of DOM on the solute water solubility and sorption coefficient.

Results and Discussion

The elemental contents of carbon, hydrogen, oxygen, nitrogen, and sulfur on a moisture-free and ash-free basis and the dry-weight ash contents for the muck, peat, and extracted peat samples used in this study are presented in Table I. The weight ratio of O + N to C is used to establish the approximate polar/nonpolar balance of the sample for later discussion. Since the sulfur content is generally low, it is excluded from the calculation of the polar group content. For the four organic matter samples studied, the oxygen content ranges from 28.9% for extracted peat to 49.4% for cellulose, and the respective carbon content from 64.0% to 44.4%.

The isotherms for sorption of benzene from water by cellulose, muck, peat, and extracted peat at 24 \pm 1 $^{\circ}$ C are given in Figure 1. The corresponding isotherms for carbon tetrachloride with these four samples are given in Figure 2. To improve the accuracy of the data and to examine the shape of isotherms, equilibrium concentrations in water (C_e) have been extended to about half the solute solubility in water or greater. Water solubilities (S_w) of benzene and carbon tetrachloride at room temperature, 1780 and 800

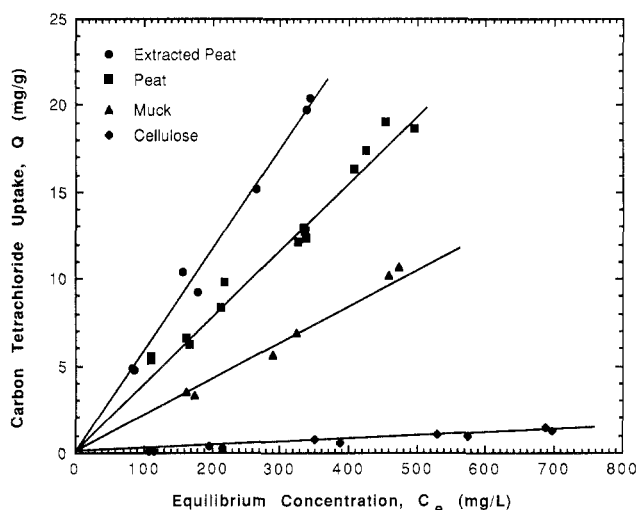


Figure 2. Uptake of carbon tetrachloride by selected organic matter samples.

Table II. Sorption Coefficients (K_{om}) and Limiting Capacities (Q_{om}^0)^a of Benzene and Carbon Tetrachloride Normalized for the Organic Matter Content of the Sorbent

material	K_{om}	benzene		carbon tetrachloride		
		Q_{om}^0 , mg/g	Q_{om}^0 , mL/kg	K_{om}	Q_{om}^0 , mg/g	Q_{om}^0 , mL/kg
extracted peat	20.8	37.1	42.2	73.5	58.8	36.9
peat	12.5	22.0	25.1	44.6	35.6	22.3
muck	7.67	13.7	15.5	27.8	22.2	13.9
cellulose	0.56	1.00	1.13	1.75	1.40	0.88

^a Q_{om}^0 (mg/g) = $K_{om}S_w$. Q_{om}^0 (mL/kg) = $K_{om}S_w/d$; where d is the solute density.

mg/L, respectively, are taken from the literature (22) for data analysis. The blank run with 1 g of peat or muck and 20 mL of 0.005 M $CaCl_2$ solution gave a DOC of ~140 mg/L. At this DOC concentration, the extent of water solubility enhancement of benzene and carbon tetrachloride and hence the effect of DOC on their sorption coefficients can be safely ignored (18, 19).

Over the concentration range covered in these experiments, the isotherms for both benzene and carbon tetrachloride are virtually linear, in keeping with findings for other organic compounds with other soils and with the partition (solubility) characteristics of solutes with SOM. Partition coefficients of benzene and carbon tetrachloride normalized for the organic matter content (K_{om}) of the sorbent are shown in Table II. For all organic matter samples except cellulose, the K_{om} value of carbon tetrachloride is greater than that of benzene by a factor of about 3.5–3.6; for cellulose, the factor is 3.1, due likely to some experimental inaccuracies in quantifying the small uptake by this sample. The difference in K_{om} between the two solutes is in good agreement with the slope of the correlation of $\log K_{om}$ vs $\log S_w$ (molar solute solubility in water) for liquid and subcooled organic compounds (3) and the difference in molar water solubility of benzene and carbon tetrachloride. The results in Figures 1 and 2 show strong dependence of the solute sorption (partition) coefficient on the composition of the organic matter sample; the K_{om} values of each solute increase by a factor of ~40 in going from highly polar cellulose to relatively nonpolar extracted peat. Garbarini and Lion (20) found similarly low K_{om} values of toluene and trichloroethylene with cellulose compared to values with soil humic and fulvic acids. Likewise, the partition interaction of DDT and other so-

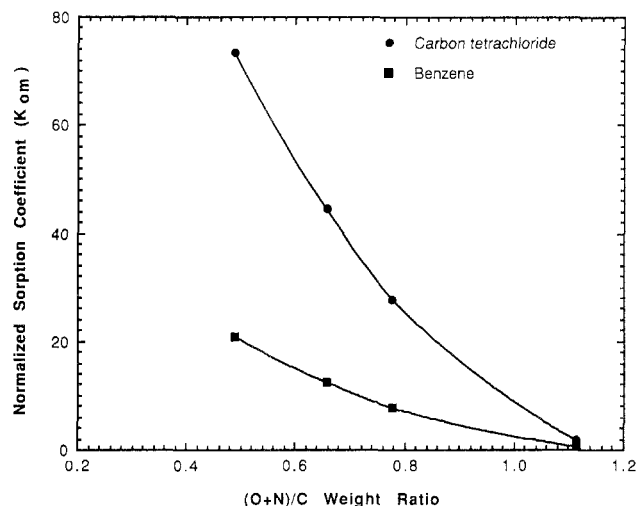


Figure 3. Plot of the normalized solute partition coefficient (K_{om}) against the (O + N)/C value of sorbent samples.

lutes with dissolved humic and fulvic acids shows a decrease with increasing polar group content of the humic material (18, 19). The effect of sample polarity on the observed partition coefficient is intimately consistent with the well-known effect of solvent polarity on solute solubility.

In addition to isotherm linearity and others as discussed, the magnitude of the observed sorption capacities for benzene and carbon tetrachloride with muck and peat is far greater than can be attributed to surface adsorption by these samples. The measured BET (N_2) surface areas of 1–2 m^2/g give about 1–1.5 mg/g calculated monolayer adsorption for these two compounds by the *dry* samples. For cellulose, which shows a limiting (saturation) capacity of ~1.0 mg/g for benzene and 1.4 mg/g for carbon tetrachloride, the observed isotherm linearity and the close relation between sorption capacity and sample polarity would also suggest solute partition to be the primary sorption mechanism; water appears to suppress the surface area of cellulose and other samples by strong polar interactions.

The influence of the organic matter polarity on the partition efficiency of benzene and carbon tetrachloride can be better visualized by plotting the observed K_{om} value against the (O + N)/C value of the sample. As shown in Figure 3, the K_{om} value rises rather rapidly as the (O + N)/C value decreases from ~1.1 for cellulose to 0.5 for extracted peat. The relative increase of K_{om} with (O + N)/C is nearly the same for both solutes. Moreover, Chiou et al. (23) showed in an earlier study that the limiting partition capacities (solubilities) of various relatively nonpolar organic liquids on a given SOM are fairly comparable, especially when expressed in liquid volume per unit weight of SOM; for respective solid solutes, the capacities are reduced in proportion to the solid activity. A similar effect for benzene and carbon tetrachloride with the organic matter samples from this study is shown in Table II. These combined effects suggest that the influence of sample polarity on solute partition coefficient should be nearly constant for various relatively nonpolar solutes. Therefore, if the increased factor in K_{om} of a relatively nonpolar solute with some SOM relative to another is known, this factor should be about the same for various relatively nonpolar compounds. As a consequence, it enables one to estimate the effect of SOM composition on K_{om} when a compositional analysis of SOM is not available.

The results in Figure 3 provide a useful basis for assessing the variability of K_{om} values of solutes with change

in SOM composition in different soils. In principle, the K_{om} values of nonpolar compounds with SOM samples that contain large amounts of undecomposed plant materials should be low compared to values with other SOM samples because of the poor affinity of these compounds with cellulosic materials. Conversely, the high polarity of cellulose should make it a good partition medium for polar liquids such as ethanol and water. As the humification process reduces the carbohydrate content of plant residue (24), it will improve the partition efficiency for nonpolar organic compounds. This effect is manifested by the higher carbon and lower oxygen contents of soil humic substances. For soil humic acid, the average elemental content is 53.8–58.7% for carbon, 32.8–38.3% for oxygen, and 0.8–5.5% for nitrogen (25), which gives 0.57–0.81 for $(O + N)/C$. Thus, although the K_{om} value of a compound is a function of the degree of humification of SOM, the K_{om} value defined by cellulose would appear to serve as the lower limit for a given solute on natural organic matter because of its extreme polar group content.

Analysis of a large set of K_{om} values with different soils shows that the variability of K_{om} values for a given compound is normally within a factor of 3 (15, 16), suggesting that the variability of SOM composition is not as large as the range of $(O + N)/C$ in Figure 3. The common assumption that SOM contains ~58% carbon (15) also implies the compositional variability in SOM among soils to be relatively small, although the actual variability is not clearly established. Taking 58% as the standard carbon content in SOM, the peat sample with 57% carbon used in this study would seem comparable in composition with SOM in "ordinary soils". For benzene, the K_{om} with this peat, 12.5, agrees well with $K_{om} = 18$ with Woodburn soil as reported by Chiou et al. (3) and with $K_{om} = 15$ with Riddles soils as reported by Boyd et al. (26). Here, the variability is relatively small, by only a factor of 1.4, suggesting that the effect of SOM from these soils is about the same as that of peat. It appears that the value of $(O + N)/C$ gives a large account for the effect of SOM polarity on the partition coefficient of a solute despite the possibility that differences in the structural aspect of SOM (e.g., the extent of aromaticity) may also influence the partition efficiency of SOM (27).

Karickhoff et al. (28) reported an average K_{oc} of 83 for benzene with the coarse silt fractions of two sediment samples, which is far greater than the values given above. This large value is beyond what may be expected from the relation of K_{om} and SOM composition given in Figure 3. For benzene to exhibit this high K_{oc} , the sediment organic matter should have extremely low polar group content, with the partition efficiency approaching that of a good organic solvent. For example, the octanol–water partition coefficient (K_{ow}) of benzene is only 135 (29). Whether the noted discrepancy results from the unique organic matter composition of the sediment samples relative to that of ordinary soils is presently not known. If such a dramatic compositional difference exists between SOM and sediment organic matter, the correlation of $\log K_{om}$ vs $\log S_w$ (3), or $\log K_{om}$ vs $\log K_{ow}$, for a set of solutes derived for soil samples would thus not apply for sediment samples. In this case, the intercept value of the $\log K_{om}$ vs $\log S_w$ correlation for soils would be significantly different from that for sediment samples, while the slope values should be more comparable.

For carbon tetrachloride, the literature lacks K_{om} data on soils for direct comparison. The consistency of the experimental K_{om} values between benzene and carbon tetrachloride in relation to their molar water solubilities

suggests that the K_{om} value of carbon tetrachloride with peat should be reasonably close to what may be expected for SOM in common soils.

In the absence of specific data on SOM composition for ordinary soils, we here consider the dependence of K_{om} on SOM composition by assigning the carbon content of SOM to be between 53% and 63%, i.e., by taking $\pm 5\%$ deviations from the normally assumed carbon value (58%). The 53% limit corresponds roughly to the lower limit of soil humic acid, which is the dominant constituent in SOM. The 63% limit applies to a hypothetical case where the SOM content of soil samples used in sorption studies has been enriched by chemical treatments in the laboratory. As the hydrogen content is relatively constant, a value of 4.8% is assigned for the calculation. The sulfur content is ignored, since it is a small value relative to others. In essence, the sum of carbon, oxygen, and nitrogen is assumed to be ~95%. By this assumption, the calculated $(O + N)/C$ value with 53–63% carbon falls into the range of 0.51–0.79. This range corresponds approximately to the difference in composition between extracted peat and muck. The K_{om} values for both benzene and carbon tetrachloride over this range vary by a factor of 2.7, which is about the magnitude of variation commonly found for organic compounds with soils. If the solute K_{om} values for individual soil samples far exceed the average K_{om} values (say, by a factor of 3 or more) from a large set of soils, one must then speculate on whether the SOM has a very unusual composition or whether the data are reliable.

In general, the K_{om} data of a single solute on soils of relatively high SOM contents usually do not differ from each other by a factor of 3 (15, 16), in agreement with the prediction obtained by assuming SOM carbon content to be 53–63%. A greater variability is found only for soil samples with very low SOM contents (<0.2%). Factors other than the SOM composition that may contribute to this enhanced variation have yet to be studied with care and rigor. In addition, the equivalency of the organic compositional effect between soil and sediment samples has not been closely evaluated. This may contribute to part of the discrepancy in K_{om} (or K_{oc}) data reported in the literature when no distinction is made between data derived from soil and sediment samples. The potential compositional difference between soil and sediment organic matters and its effect on solute partition efficiency will be the subject of further investigations.

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Registry No. C_6H_6 , 71-43-2; CCl_4 , 56-23-5; cellulose, 9004-34-6.

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Solubilization of Zinc Oxide from Filter Dust with *Penicillium simplicissimum*: Bioreactor Leaching and Stoichiometry

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■ Filter dusts from metal-processing industries contain valuable metals which should be recycled. Some disadvantages of conventional recycling methods can be avoided by applying biohydrometallurgical methods. Fungi are suitable for such processes because they are fairly resistant to heavy metals. Furthermore, leaching activity occurs in a pH range from 2 to 7. This is important because filter dusts generally raise the pH of the medium. Leaching of zinc from zinc oxide contained in filter dust was possible in a bioreactor (stirred tank reactor) especially constructed for this purpose. Zinc solutions of 0.41 M were obtained after 9 days of leaching. The zinc concentration was doubled compared to leaching experiments in shake-flask cultures. The solubilization of zinc oxide was caused by the action of protons originating from citric acid produced by the fungus. A further increase in solubilized zinc seemed difficult to achieve, because zinc and citric acid precipitated at the high zinc and citric acid concentrations present at the end of the leaching period. The lack of a cheap growth substrate for the fungus appeared to be the greatest handicap toward an application on an industrial scale.

Introduction

Large amounts of filter dusts develop during pyrometallurgical processes of winning metals. These mixtures

of metal oxides are of great economic value (1). For example, the filter dust used in this work contained 50% zinc, 20% lead, and 6% tin, on average. Pyrometallurgical as well as hydrometallurgical recycling shows some disadvantages (1): (i) recovery rates are low and it is difficult to win the metals in a pure form; (ii) costs of chemicals and of precautions against environmental pollution are high; (iii) an economic recycling process is only guaranteed if a high turnover is possible. The use of biohydrometallurgical recycling methods is intended to avoid some of these disadvantages. Important characteristics of leaching processes with microorganisms are as follows: (i) the pollution of the environment is negligible; (ii) a selective extraction of metals is possible in certain cases; (iii) the costs of chemicals are low when autotrophic bacteria can be used for leaching processes, or when organic wastes can be used as growth substrates for heterotrophic microorganisms; (iv) energy requirements are low.

The leaching of zinc from filter dust of a copper smelting plant turned out to be possible with the fungus *Penicillium simplicissimum* (2). The filter dust consisted of a mixture of metal oxides, half of which being zinc oxide. About 80-90% of the total zinc was solubilized after 6-10 days of cultivation in a shake-flask culture (25 g/L filter dust; 13 g/L zinc in solution at the end of the leaching period). Leaching was caused by the action of protons originating from citric acid excreted by the fungus (3). Zinc and, to a minor extent, copper and lead were solubilized whereas tin was not solubilized at all (3). In the medium used, the fungus produced considerable amounts of citric acid only

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