The technical details of the hydrothermal method were reported earlier[9-11]. In the present study, the two starting solids used were molybdic acid H_2MoO_4 (Analar, Wilson) and molybdenum trioxide MoO_3 (Analar, Glaxo). The fluid used with the solids was distilled water. The charge was sealed in platinum capsules. Details of the experimental runs are given in Tables 1 and 2, and the corresponding plots for H_2MoO_4–H_2O and MoO_3–H_2O systems are given in Figures 1 and 2 respectively. In the H_2MoO_4–H_2O system, molybdic acid directly decomposes to MoO_2 at low pressures (< 1.5 kbar), but in the high-pressure region (> 1.5 kbar) the white molybdic acid transforms into a blue oxide phase and then to MoO_2. The blue oxide phase was slightly soluble in water, hence yield was poor. Besides it was admixed with a white molybdic acid phase and therefore identification and analysis of this phase were unsuccessful. Both molybdic acid and blue oxide phases, when directly heated in air, transform to MoO_2, which, further, sublimates at 800°C. The MoO_2 in this system invariably appeared as radiating tabular crystal aggregates. In the MoO_3–H_2O system, the blue phase is found at pressures lower than 0.5 kbar. There is a progressive change in colour of the blue phase as well as in the relative intensities of certain reflections in the X-ray powder diffraction data with increasing temperature of the run. These changes may be due to the varying valence state of molybdenum in the blue oxide with the corresponding oxygen nonstoichiometry. Attempts to determine the oxygen content of the blue oxide by heating it under oxygen atmosphere until it converted to MoO_3 were unsuccessful because of the minute oxygen deficiency which is beyond the measuring accuracy of the normal thermogravimetric methods. MoO_2 in this system appeared as good stubby crystals. Scanning electron micrographs of MoO_2 crystals obtained in the two systems are shown in Figure 3.

We feel that phase diagrams provide useful information for synthesis of molybdenum-based mixed oxides with both 6^+ and 4^+ valence states of molybdenum with well-controlled oxygen stoichiometry, because of the constant intrinsic oxygen fugacity in the hydrothermal system and the relatively low temperatures involved.

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A study on Palamau vermiculite with special reference to its metal-adsorption properties

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Vermiculite-hydrobiotite is a hydrated magnesium aluminium iron sheet silicate of variable chemical composition. X-ray diffraction study of samples of mineral deposit shows that the material consists of unaltered biotite, hydrobiotite and vermiculite. We also present chemical composition determined by microprobe analysis. Vermiculite also has useful metal-adsorption properties and can be used as a low-cost adsorbent. Zinc removal by vermiculite is pH-dependent and is higher in alkaline medium. Vermiculite may also be useful as an adsorbent for removal of other metal pollutants.

THE mineral is flaky and yellowish-brown to brownish-grey, with a subpearly to submetallic lustre. It occurs as soft, pliable, inelastic laminae, often showing negative optical character and small axial angle. The hardness (Moh's scale) ranges between 1 and 2, while the specific gravity varies between 2.36 and 3.20. Vermiculite mostly resembles the low-grade micas, but differs by its characteristic of being expanded at an angle of 90° to the cleavage plane when heated above 200°C. Expansion or exfoliation occurs when vermiculite is rapidly heated to about 1000°C and maintained at that temperature for a few seconds so that part of its combined water is expelled. The most striking characteristic is that, when exfoliated, the colour changes from brown to glittering gold, silver tint or bronze, which confers insulation against radiation. Vermiculite exfoliates without any change of colour when treated with hydrogen peroxide. When vermiculites are refluxed for about three hours with a 1:2 mixture of sulphuric acid and water, milky-white pure silica flakes are liberated, confirming that the sample is vermiculite and not biotite. Thus vermiculite can be differentiated from biotite by the exfoliation and refluxing test and by treatment with hydrogen peroxide. The rate of

expansion of the samples collected from various locations is different owing to the presence of hydrobiotite with vermiculite in different proportions.

The samples of vermiculite-hydrobiotite were collected from Biwabathan (23° 55′ N, 84° 4′ E), Palamau district, Bihar. The mineral deposit is associated with amphibolites and magnetites at the contact of pegmatites and quartz veins. It occurs as veins, lenses and pockets of various dimensions within the host rock. The mineralization is post-kinematic with reference to F_1 folds and pre- to syn-kinematic with regard to F_2 folds. The vermiculite mineralization is thus controlled by both lithology and structure.

X-ray diffraction (XRD) analyses of two representative samples of vermiculite were carried out using a Rigaku diffractometer at a scanning speed of $2°\,2\theta$/min and Ni-filtered Cu Kα radiation at 35 kV and 20 mA. The results are shown in Figure 1. The strong basal reflection at 10.04 Å is due to hydrobiotite[1]. In all the samples studied hydrobiotite is the major phase, invariably associated with biotite and vermiculite. Since the samples contain a certain amount of alkalies, the basal spacing at 14 Å for vermiculite could not be observed. The XRD peaks indicate that the transformation of biotite to vermiculite is incomplete, hydrobiotite peaks being the prominent ones. Hydrobiotites, which have mixed layers of biotites and vermiculites, always have smaller basal spacing than natural vermiculite, but vermiculites with interlayer Na^+, Cs^+, NH_4^+ have a basal spacing close to that of hydrobiotite[2]. Thus XRD analysis of the samples indicates an interstratification of single and double layers of biotite and vermiculite.

Table 1 gives the chemical compositions of four representative samples of hydrobiotite. The analysis was carried out using a JEOL JXA-35 electron probe microanalyser employing a wavelength dispersive spectrometer and the Bence and Albee[3] data-reduction procedure. Microprobe analyses reveal high proportion of silica (39.97%), comparatively low alumina (16.04%),

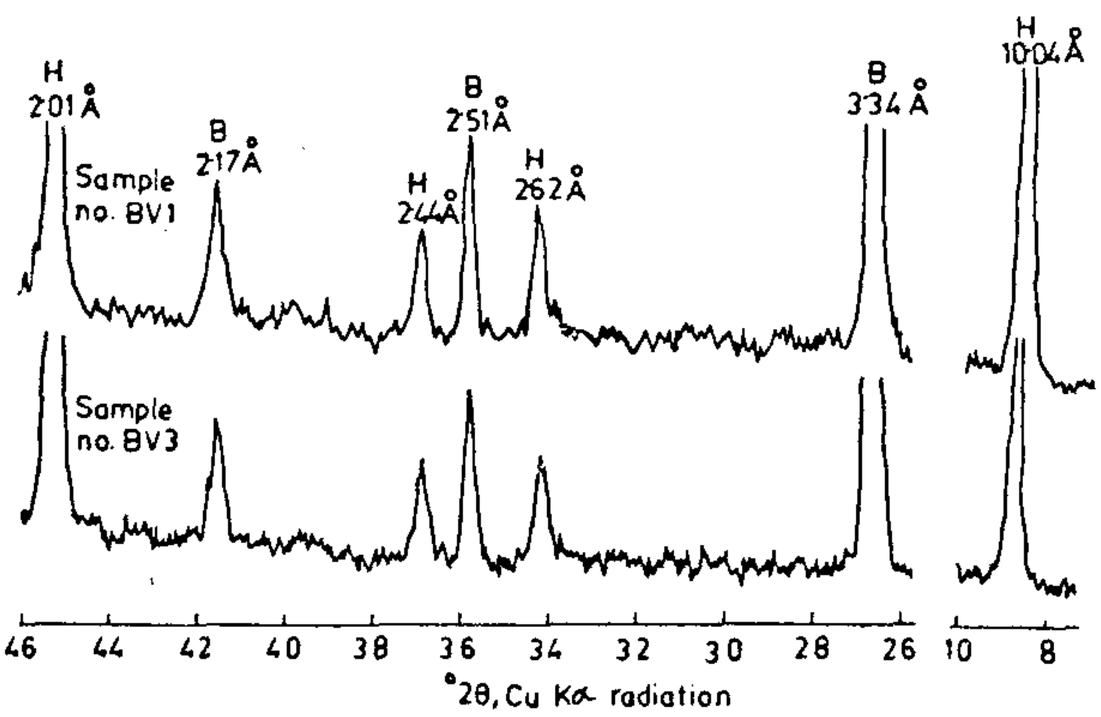

Figure 1. X-ray powder diffraction pattern of vermiculite samples BV1 and BV3. H, hydrobiotite; B, biotite.

Table 1. Microprobe analysis of vermiculite-hydrobiotite samples.

Sample	SiO_2	Al_2O_3	MgO	FeO*	MnO	K_2O	H_2O
BV1	40.13	17.99	12.04	8.73	0.14	9.14	11.83
BV2	39.71	19.87	11.38	9.43	0.14	10.45	9.02
BV3	37.94	12.73	18.84	9.35	–	8.70	12.44
BV4	42.11	13.56	21.27	8.39	–	9.43	5.24

*Total Fe
–, Not obtained

near-absence of manganese, high proportion of alkali (9.43%), and a considerable amount of combined water (9.63%). As the samples contain high percentage of alkali, vermiculitization does not appear to be complete.

Thus the field and laboratory studies show that the mineral is derived from the hydrothermal alteration of biotite. In most of the cases, the alteration of biotite being partial and the average exfoliation being only ten times, the name hydrobiotite (biotite-vermiculite) is found to be more appropriate for the mineral.

The cation-exchange capacity (CEC) of vermiculite was determined by the conventional method[4] and was found to be 62 meq/100 g.

Zinc at higher than 5 mg l^{-1} in the aquatic environment is detrimental to living organisms. Much work has been done to study the heavy metal-adsorption properties of natural materials such as laterites, river sediments and soil[5–7]. In India, vermiculites are mainly used in false roofing, wall decoratives and insulation work, but their potential as natural adsorbent has never been explored. Here we report the results of experiments on metal-adsorption properties of vermiculite.

Zinc-removal studies were conducted in batch experiments at room temperature. Two grams of vermiculite (1.0 mm geometric mean dia.) was taken in several 250-ml glass beakers. Zinc-spiked distilled water (100 ml) was added, and the beakers were kept on a rotary shaker. The beakers were removed from the shaker after different periods of contact time. The adsorbent was separated by gravity settling and the supernatant analysed for zinc using an AA-670 flame atomic absorption spectrophotometer. Standard zinc (1 g l^{-1}) was prepared from zinc chloride in double-distilled water; pH was adjusted with 0.1 N HCl or 0.1 N NaOH as required.

Zinc removal by vermiculite is shown in Figure 2. Removal was rapid initially, slowed markedly between 2 h and 6 h, and gradually approached equilibrium. At the beginning of the process, when there are available exchange sites on the mineral, the zinc is sorbed at a high rate. The removal of zinc by vermiculite can be described as an ion-exchange process. The interlayer cations (Mg^{2+} or K^+) in the vermiculite may be exchanged for the zinc cations present in the solution.

The pH of the suspending medium plays an

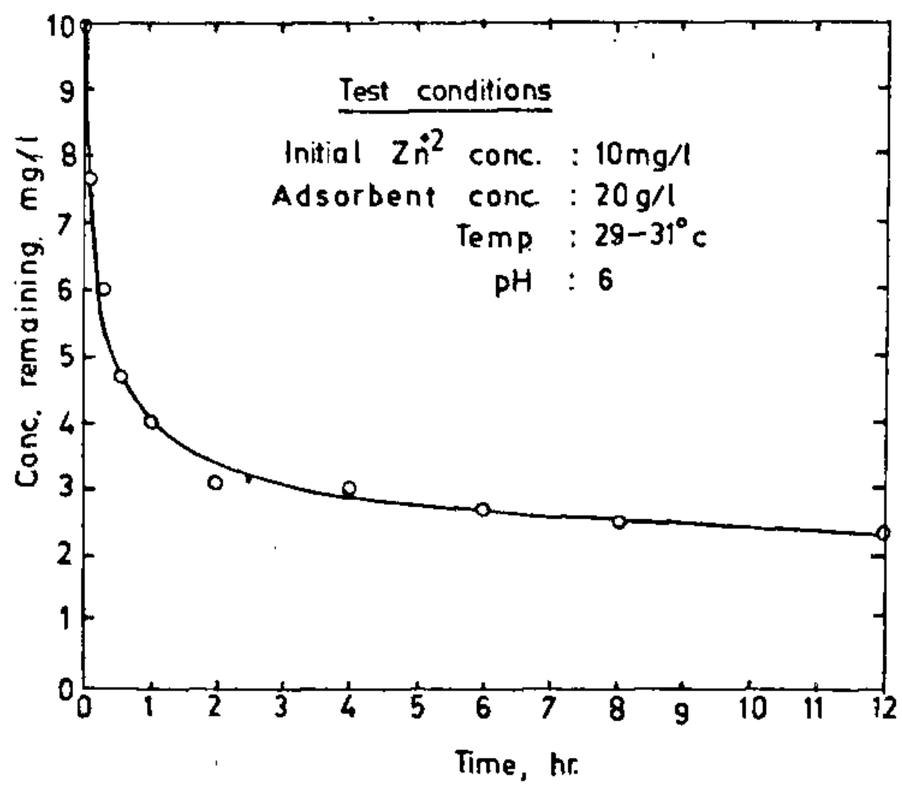

Figure 2. Kinetics of zinc removal by vermiculite.

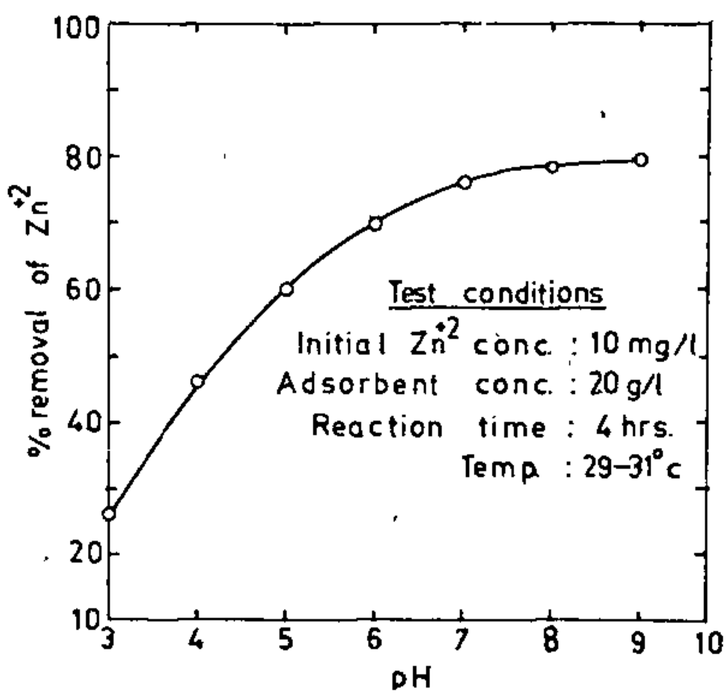

Figure 3. Effect of pH on zinc removal by vermiculite.

important role in the adsorption of heavy metals by clay minerals. Figure 3 shows the effect of pH on removal of zinc by vermiculite. At pH 3.0, only 26% of the zinc present was removed; the rate increased with increase in pH, and at pH 9.0 about 80% of the zinc was removed. This type of behaviour is particularly true for the strongly hydrolysable cations[8]. At low pH, the H^+ present in the solution competes with zinc for the active sites on the vermiculite. The enhancement of adsorption with increase in pH, is apparently due to the presence of coordinated OH^- groups. The replacement of an aquo group by a hydroxo group in the coordination sheath of a metal atom may render the complex more hydrophobic by reducing the interaction in the solvent–hydroxo complex. Complex interaction might then in turn enhance the formation of covalent bonds between the metal atom and specific sites on the solid surface by reducing the energy required to displace water molecules from the coordination sheath[9]. It has also been reported[10] that clay minerals generally exhibit strong cation-exchange properties in alkaline solution, strongly binding many hydrolysable metals to their surfaces.

On the basis of this study, we conclude that vermiculite may be extensively used for removal of zinc, one of the pollutants in industrial effluents.

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Savannization of dry tropical forest increases carbon flux relative to storage

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A study of dry tropical forest and savanna derived from it suggests that, although carbon stored in the savanna vegetation was less than half of that in the forest, carbon input through net primary production was similar. The savanna, drawing upon biodiversity resources, was able to maintain the same level of ecosystem productivity as the forest through species replacement. Belowground parts contributed more to carbon storage and flux in savanna than in forest, but carbon stored in soil remained far lower in savanna. Our studies indicate that conversion of dry tropical forest into savanna increases carbon flux relative to storage. This has implications for global carbon budget studies.

GLOBAL carbon dioxide concentrations have substantially increased from the mid-eighteenth century to the present day[1], and CO_2 is expected to reach 600 ppm before the middle of the next century[2]. Deforestation accounts for an annual net release of carbon[3] between