The Interaction of Molybdenite and Aqueous Copper(II)

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Conditioned (or secondary) copper deficiency in ruminants is a widespread problem and in most instances occurs when dietary copper is not low but when certain dietary factors exist which inhibit copper absorption [1]. Among the various antagonists of copper metabolism, the most powerful known is the tetrathiomolybdate anion [2]. The mechanism by which this species renders copper unavailable to the animal is as yet unknown. Antagonistic trace elements in general hinder copper utilization by lowering its solubility in the intestinal lumen, by competing during its absorption or transport or by altering its distribution between body tissue receptors [3].

However, in ruminant species it is well known that a simple two way interaction is not responsible but a third species, namely sulphur or some derivative of sulphur, also participates, thus reducing copper availability.

Exchange reactions involving sparingly soluble metal sulphides and aqueous copper are important in other areas as well, such as mineral activation in the mining industry, with aqueous copper(II) solutions being utilized prior to reaction with xanthate collectors and subsequent flotation [4].

As part of a general study on a number of metal sulphides, we have investigated the interaction between copper(II) and both synthetic and natural molybdenite, and we wish to report the formation of a copper–molybdenum intermediate species formed in alkaline conditions.

Experimental

Synthetic molybdenum disulphide, MoS_2(syn), was prepared by literature methods [5], while natural molybdenum disulphide, MoS_2(nat), was provided by the Climax Molybdenum Company.

The interaction of the sulphides with copper(II) was studied in aqueous solution at different pH values. Aliquots (*ca.* 150 cm^3) of a freshly prepared solution of copper(II) sulphate (7.85×10^{-5} M) were adjusted to the required pH using dilute sulphuric acid or dilute sodium hydroxide. The pH was monitored with a Corning 12 expanded-scale pH meter. 50 cm^3 portions of these solutions were added to flasks which contained MoS_2 (0.0315 g, 1.97×10^{-4} M). All the flasks were stoppered and shaken at 200 rpm for 24 hours. The temperature was maintained at 25.0 ± 0.1 °C using a water bath. Control flasks containing only copper(II) were treated in a similar way. Both control and reaction flasks were filtered at the end of the reaction period using Whatman 42 ashless filter paper. Metal ion concentrations of the filtrates were determined by flame atomic absorption spectroscopy, using a Perkin-Elmer 2280 instrument. The degree of Cu^{2+}(aq) adsorption by MoS_2 was calculated using eqn. (1).

$$\frac{C - T}{C} \times 100\% \qquad (1)$$

where C is the concentration of Cu^{2+}(aq) in the control solution, and T is the concentration of the Cu^{2+}(aq) in the test solution.

Specific surface areas (*SSA*) of the powders were determined using a volumetric absorption apparatus [6], with N_2(g) as the absorbate. X-ray powder diffraction photographs were obtained using a Nonius, Guinier-de Wolff quadrupole focusing powder camera, with a Cu Kα X-ray source. UV–Vis spectra were recorded on a Perkin-Elmer 552 spectrophotometer, and infrared spectra were recorded in the 4000–300 cm^{-1} range, as nujol mulls or KBr discs, on a Perkin-Elmer 683 spectrophotometer.

All the chemicals used were of AnalaR grade. MoS_2(nat) was used without further purification.

Results and Discussion

Initially the two molybdenum disulphide species were treated in the same way. However, although a reaction with MoS_2(syn) was observed and fairly dramatic changes in pH were noted, there was apparently no reaction with MoS_2(nat). Several samples were used but indications were that the MoS_2(nat) was inert to copper(II) interaction, under these conditions.

The interaction and adsorption between MoS_2(syn) and Cu^{2+}(aq) was investigated at different pH. The results are shown in Fig. 1, and clearly demonstrate that different reactions are occurring at low pH and at higher pH (>6).
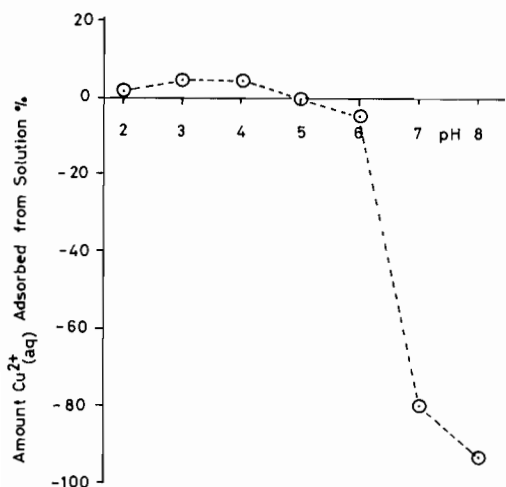
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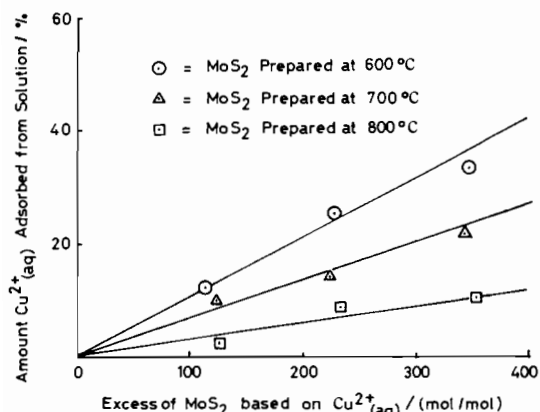Fig. 1. Effect of pH on amount of Cu^{2+}(aq) adsorbed by MoS_2(syn).

Fig. 2. Dependence of Cu^{2+}(aq) adsorption on synthesis temperature of MoS_2 at pH = 3.
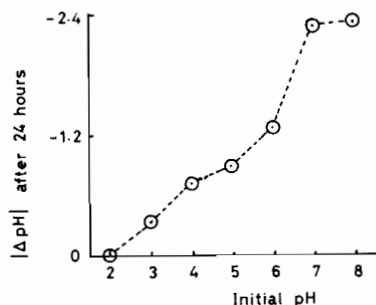

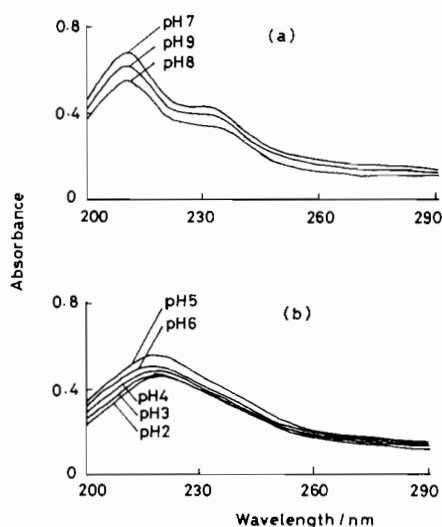Fig. 3. ΔpH in the MoS_2/Cu^{2+}(aq) interaction, after 24 h.

Fig. 4. (a) UV spectra of test solution filtrates, at pH 7, 8 and 9; (b) UV spectra of test solution filtrates, at pH 2, 3, 4, 5 and 6.

Below pH = 6, the Cu^{2+}(aq) is adsorbed from solution, with a maximum at about pH = 3. However, the reaction is dependent on the temperature of synthesis of MoS_2. When the temperature is closely controlled, a more active material is produced at lower temperatures, Fig. 2. The lower the temperature of synthesis the more copper is adsorbed.

The *SSA* of the synthesised materials was determined and it was found that lower temperatures of synthesis yielded greater *SSA* values. The MoS_2 prepared at 600 °C, 700 °C and 800 °C had *SSA* values of 8, 6 and 4 $m^2 g^{-1}$ respectively. This effect has been shown before for nickel oxide [7]. The remaining experiments were standardised to use MoS_2 prepared at 700 °C.

It can be seen that the amount of copper(II) adsorbed from solution is comparatively small and reaches a maximum at around pH 3 (Fig. 1). We have determined ΔpH in the MoS_2/Cu^{2+}(aq) interaction (Fig. 3). A drop in the pH is observed and this is due

to the interaction of MoS_2 with water, and is independent of the Cu^{2+}(aq). Such an effect is not unknown as a similar drop in pH on grinding molybdenite in a water suspension was attributed to the formation of sulphurous and sulphuric acids [8]. When pH > 6, aqueous copper(II) forms the insoluble hydroxide. Consequently filtered copper(II) solutions at this pH contain very little aqueous copper(II). The redissolution of this hydroxide in the test solutions is probably also due to acid formation. The ultraviolet spectra of the test solutions, showing λ_{max} at about 212 nm for pH 7, 8 and 9, and at about 221 nm for lower pH values. These values were compared to the values obtained from the ultraviolet spectra of pH adjusted MoS_2 suspension filtrates and Cu^{2+}(aq) filtrates, in the same pH range, and were found to be sufficiently different to conclude that neither of these solutions were responsible for the new peaks shown in the test spectra.

It is apparent from the spectra (Fig. 4) that an interaction has occurred at pH > 6 and that the product is responsible for the emergence of the new peak and shoulder (Fig. 4(a)). This interaction is

obviously pH dependent. At pH < 6 the Cu^{2+}(aq) adsorption occurs, at the liquid surface interface, as shown by the MoS_2 surface area dependency. Above pH of 6, the MoS_2–Cu^{2+} interaction results in the formation of a soluble product, identified by its UV spectrum. X-ray powder diffraction photographs of MoS_2 samples both before and after interaction with Cu^{2+}(aq) were identical at all pH values studied, but the very low concentrations of Cu^{2+}(aq) would preclude any surface product analysis.

It is possible that this method of synthesis [5] produces an oxide layer, at least in part, on the surface. This may be responsible for the different reactivity observed in the two molybdenum disulphides, MoS_2(syn) and MoS_2(nat). This layer could be formed at one of several stages. On heating the reactants and product in air the formation of molybdenum trioxide, MoO_3, has been reported [9]; MoS_2 samples require grinding following formation by the above method, and again the trioxide has been suggested as a product on prolonged grinding [9]; MoS_2 undergoes oxidation in the presence of water [10], eqn. (2) and the final stage of the preparation involves washing the product to free it of residual reactants.

$$MoS_2(s) + H_2O \longrightarrow MoOS_2(s) + H_2 \qquad (2)$$
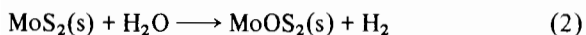
If the oxide layer is responsible, for mediating this reaction, then the most likely product formed would be a heteropolymolybdate species. The oxide layer would dissolve at high pH to give a molybdate [11], which would polymerise as the pH drops, and the extent of polymerization is pH dependent [12]. Currently, we are attempting to characterise the product of this interaction. Some of the problems associated with the system include the presence of many salts in the filtrate after reaction and the immediate precipitation of insoluble copper molybdate on heating the filtrate. The latter material was identified using infrared spectroscopy.

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