MODELS FOR TETRACYCLINE IN AQUATIC ENVIRONMENTS

II. Interaction with Humic Substances

B. B. SITHOLE and R. D. GUY*

Trace Analysis Research Centre, Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada, B3H 4J1

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Abstract. The adsorption of tetracycline onto humic acid and peat has been found to obey the Freundlich and Scatchard plot models. The latter model showed that the adsorption was biphasic in nature thus indicating the presence of two types of binding sites on the organic matter. The adsorption was reduced at high ionic strength and pH.

1. Introduction

Numerous microorganisms are found in soil. Under suitable conditions of temperature, moisture and nutrients, the micro-organisms multiply very rapidly producing by-products which include antibiotics one of which is tetracycline (from *Streptomyces aureofaciens* strain (Tamm, 1977)). Tetracycline is often used as an additive in animal feeds to combat various disease producing bacteria. Concern has been expressed that continuous leaching of antibiotics in feedstuffs into the environment leads to the emergence of resistant species. Thus it is important to obtain information on the transport of the antibiotics in the soil and aquatic environments.

This report is concerned with the interaction of tetracycline with soil organic matter, that is, peat and humic substances. In the first paper of this series the interaction of tetracycline with clay materials indicated that a clay coated with tannic acid had a higher adsorption capacity than Na and Ca forms of the clay. The interaction of tetracycline with pure clay indicated that two types of interactions were responsible for adsorption – the binding of tetracycline to divalent cations in the double layer of the clay and the interactions between alumina groups at the clay edges with polar functional groups on tetracycline. The interaction between tetracycline and the tannic acid form of the clay was thought to be due to H bonding between the tetracycline and the phenolic groups on the tannic acid molecule. Soil organic matter has carboxyl and phenolic groups that may interact with the polar groups on tetracycline in a similar fashion as the tannic acid bound to the clay of the earlier study.

2. Experimental

The materials and methods used in this study have been described fully in previous reports (Sithole and Guy, 1985, 1986; Guy and Narine, 1980). The peat was collected

* Author to whom correspondence should be addressed.

from a peat bog in Nova Scotia. About 100 g of the material oven dried at 70 °C after which it was ground in a micro-mill. Humic acid was obtained from Aldrich. The adsorbants were suspended in 2M HCl overnight to remove metal contaminants and to convert the samples to the protonated form. The adsorbants were collected by filtration, washed with distilled water until no chloride could be detected with silver nitrate, and dried at 70 °C.

The total acidities of the adsorbants were determined (Schnitzer and Khan, 1972) to be 6.7 meq g⁻¹ and 5.1 meq g⁻¹ for peat and humic acid, respectively.

A dialysis separation was used to evaluate the amount of tetracycline adsorbed onto the organic matter. The advantage of dialysis separations using 12000 MWCO membranes was that organic matter solubilized from the peat or humic matter could not pass through the membrane. The solubilized organic matter will not interfere with the differential pulse polarography measurements (adsorption of humic substances and or surfactants onto the mercury drop will interfere with the electrochemical measurements) of the dialyzate. This type of separation also permits one to consider all of the tetracycline that does not pass through the membrane as bound to soil organic matter, that is, tetracycline bound to the particulates and tetracycline bound to dissolved organic matter. A preliminary run was done to determine the time necessary to attain equilibrium. Tetracycline was added to a suspension of peat or humic acid and samples were removed at periodic intervals over 48 hr. The suspension was filtered through a 0.20 μm membrane filter and the free tetracycline in the filtrate determined by differential pulse polarography. The kinetic run indicated that adsorption equilibrium was attained within 24 hr. Dialysis equilibrium was attained within 8 hr so the samples were left for 24 hr prior to analysis.

Individual adsorption experiments employed 250 mL tetracycline solution and peat or humic acid particulates. The adsorption was studied as a function of mass of adsorbant, type of adsorbant, pH and the ionic strength of the suspension.

3. Results and Discussion

The adsorption of tetracycline onto the humic acid and peat particulates required about 18 hr to attain equilibrium. This equilibration time was much longer than the 30 min necessary for the equilibration with the clays (Sithole and Guy, 1986) or 3 hr necessary for the equilibration of paraquat with humic materials (Burns et al., 1973). This suggests that the binding of tetracycline to the organic particulates may involve the slow diffusion of the tetracycline in the peat and humic acid matrix. The binding of tetracycline to the clays was to surface and edge sites therefore the equilibration was more rapid.

A preliminary study of the binding of tetracycline to the peat and humic acid particulates indicated that over the concentration range of interest (1 to 10 ppm tetracycline) 10 to 90% of the tetracycline remained in solution if the particulates were present at a level of 500 μg of particulate per millilitre of suspension. Figures 1 and 2 present the adsorption isotherms for the binding of tetracycline to humic acid and peat, respectively. The isotherms in Figures 1 and 2 illustrate the effect of suspension pH on