

## Copper(II) Adsorption by Waste Tea Leaves and Coffee Powder

W.T. TAN

Chemistry Department,  
Faculty of Science and Environmental Studies,  
Universiti Pertanian Malaysia,  
Serdang, Selangor, Malaysia.

**Key words:** Uptake; pH; concentrations; competitive reaction; adsorption; chelation.

### ABSTRAK

Bahan-bahan minuman yang telah digunakan seperti serbuk kopi dan daun teh daripada hasil tempatan didapati berkebolehan mengasingkan ion-ion kuprum(II) daripada larutan akuas. Ciri-ciri pengambilan Cu(II) oleh hampas bahan-bahan minuman tersebut dikaji secara sistematik. Didapati pengambilan Cu(II) ini bergantung pada pH, kepekatan logam, sifat-sifat fizikal substrat dan kekuatan ion. Ion-ion/molekul-molekul yang bersaing seperti Pb(II) dan bahan aktif permukaan seperti Triton X-100 mengganggu proses pengambilan kuprum. Kadar pengambilan ini bertambah mengikut pH dan untuk kedua-dua bahan tersebut julat pH bagi pengambilan maksimum ialah antara 5-7. Pergantungan kepekatan logam Cu(II) mengikut "Isotherm Langmuir." Keputusan-keputusan didapati selaras dengan mekanisma-mekanisma yang mana pengambilan Cu(II) ini adalah disebabkan oleh serapan ion spesifik melalui pengkelatan dan tindakbalas pertukaran ion.

### ABSTRACT

The consumed coffee powder and tea leaves of local produce were found to be able to remove substantial amounts of Cu(II) ions from aqueous solution. The characteristics of Cu(II) uptake on these beverage waste were systematically investigated. It was found that the Cu(II) uptake was dependent on pH, metal concentration, physical nature of substrate and ionic strength. Competing ions/molecules such as Pb(II) and surfactant such as Triton X-100 interfere in the uptake of Cu(II). The degree of uptake increases with pH and the pH range for maximum uptake was found to be 5-7 for both wastes. Metal concentration dependent assumed a Langmuir Isotherm. The results obtained were found to be consistent with the mechanisms that Cu(II) uptake was due to specific ion adsorption via chelation and some degree of ion-exchange reaction.

### INTRODUCTION

Man's awareness of the importance of waste utilization and the detrimental effects of heavy metal pollution has led to considerable research efforts aimed at understanding the interaction of metal with wastes and hence the ultimate use of wastes for the removal of heavy metal from wastewater. Several natural and waste polymeric materials have been demonstrated to remove heavy metals from wastewater. They include bark waste (Randall 1974), waste tire rubber (Netzer *et al.*, 1974; Knocke and Hemphill, 1981), 'activated carbon' (Netzer and Norman,

1973) and peat moss (Chaney and Hundemann, 1979). Other naturally occurring media possessing metal removing capability are clay (Huang *et al.*, 1977; Farrah and Pickering, 1976, 1977), hydrous iron and manganese oxides (Guy *et al.*, 1975; Posselt *et al.*, 1968).

From the literature, several possible interactions responsible for the uptake of metal can be readily discerned:

- metal chelation by organic matter such as in peat moss (Chaney and Hundemann, 1979),
- metal-clay colloid ion exchange reaction such as in clay (Guy *et al.*, 1975),

- c. metal-disulfide bonding such as in waste rubber (Netzer *et al.*, 1974; Knocke and Hemphill, 1981).

The extent of the metal substrate (waste) interaction are in general dependent on pH, metal concentration, presence of competing metal ions, ionic strength and nature of substrate.

It has been suggested that the metal uptake capacity of peat moss is due to the chelating properties of its constituents especially lignin and cellulose. These materials constitute the major constituents of the cell walls and possess polar functional groups such as alcohols, aldehydes, ketones, carboxylic acids, phenolic hydroxides and ethers. The polar nature of these complex materials can remove large quantities of metal ions from aqueous solutions (Chaney and Hundemann, 1979). Since the chemical composition of the insoluble cell wall for tea leaf and coffee wastes are largely made up of cellulose, lignin and some structural proteins (Table 1) (Harler, 1963; Sivetz, 1963), its use for metal removal should be feasible.

In Malaysia, like in many other countries, tea and coffee are the traditional drinks of most Malaysian adults. Usually, the locally produced tea leaves and roast coffee or its powder are sold in disposable bags. The normal practice after the brewing of tea and coffee in hot water is to dispose off it as waste. These wastes usually constitute part of the household waste. Although

TABLE 1a  
Percentage composition of the ethanol insoluble material of black tea (dry weight basis) (Harler 1963).

Constituent	Percentage
Cell wall material	46.8
Hot water-soluble polysaccharide and proteins	9.6
Hot water insoluble proteins	12.1
Lignin and structural proteins	14.7
Cellulose	37.2

TABLE 1b

Chemical composition of the insoluble portion of roast coffee (dry weight basis) (Sivetz 1963)

Constituent	Percentage
Carbohydrate (43%)	
Caramelized sugars	7
Hemi-cellulose (hydrolyzable)	14
Fiber (not hydrolyzable)	22
Oils	15
Proteins	11

their contribution as solid wastes to the environment is not significant (Moore and Moore 1976), its potential re-use for other purposes like metal removal should not be overlooked. However, before this can be fully realized, the characteristics of the metal uptake by these wastes should be studied in some detail.

The present studies were designed to investigate systematically the uptake characteristics of copper (II) by tea leaves and coffee powder wastes. Each waste beverage was studied separately to determine its metal uptake characteristics as a function of pH, metal, ionic strength, physical nature of the substrate and in the presence of surfactant and competing metal ions.

## MATERIALS AND METHODS

### *Apparatus*

In International Laboratory double beam atomic absorption spectroscopy (model 651) was used for the analysis of copper content of the solutions. The simultaneous analysis of copper and lead contents of the solutions was carried out by a Princeton Applied Research Polarographic Analyzer, Model 384 equipped with static Mercury Drop Electrode (Model 303) using differential pulse mode at 2mV/S, and pulse amplitude of 50mV. The orion pH meter (Model 601) was used to determine the pH of the solutions.

*Treatment of Tea and Coffee Waste*

Both the tea leaves and coffee used in the studies are processed and distributed by local companies.

Tea leaves and roast coffee (coarse grain) were brewed in hot water for 10 minutes. The used tea leaves were then removed from its bags and dispersed in dilute acid solution ( $10^{-2}$  M  $\text{HNO}_3$ ) for two hours. They were then filtered and washed with deionised distilled water (DDW). (DDW was prepared by running laboratory distilled water through Millipores purification system once before use). This process of cleaning and filtering was repeated when necessary to remove any metal ions and acid adhering to the tea wastes. The residue was air dried in the sun. The used coarse grain coffee was air dried and powdered into smaller grains by using mortar and pestle. The resulting coffee powder was then subjected to the same cleaning treatment given to tea waste. For most studies, air dried samples were used. However, wastes which were activated in the oven at  $110^\circ\text{C}$  for two hours were also used for some studies. The grain size of tea leaves waste as determined by U.S. Standard sieve was 60 mesh, and that of coarse coffee and powdered coffee were 20 and 80 mesh respectively.

*Procedure*

The uptake of copper by the separate waste beverages was studied by adding a known quantity of the treated tea leaves and coffee powder wastes to metal ion solutions having initial metal concentration of 0–25.0  $\mu\text{g}/\text{ml}$  in 50.0 ml sample solutions. A total of 100 ml copper solution was prepared and divided into two equal portions of 50 ml.

One portion is used as control (i.e. one without added substrate) while substrate is added to the other. The containers used were polyethylene bottles of 100 ml capacity. The mixture was shaken for four hours followed by decantation or filtration (when necessary) and metal analysis. The difference between the control reading and sample readings (with

waste) was taken as the amount of metal taken up by the waste. Four hours was found to be sufficient for the equilibrium uptake of metal by the substrate.

The effect of pH on the metal uptake process was studied by introducing 30 mg waste beverage to 50.0 ml of 2 ppm Cu solution at different pHs of between 1 and 3 (adjusted by  $\text{HNO}_3$ ), 4 and 6 (adjusted by  $10^{-3}$  M potassium acetate) in  $1.0 \times 10^{-2}$  M  $\text{KNO}_3$ ,  $10^{-3}$  M  $\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4$  and  $10^{-3}$  M  $\text{NH}_3/\text{NH}_4\text{Cl}$  were used as buffers for pH 7 and pH  $> 7$  respectively. Ionic strength was maintained at a constant level by using 0.10 M  $\text{KNO}_3$ . The metal uptake studies were carried out at different values of ionic strength set by  $\text{KNO}_3$  from 0.001 M to 0.50 M  $\text{KNO}_3$  and different amount of strong surfactant set by Triton  $\times 100$  from 0.0001 to 0.002% (V/V). With the exception of reproducibility studies, all the other studies were carried out once experimentally. The reproducibility study on the percentage of Cu uptake by 30 mg tea waste from 50 ml solution of 2 ppm Cu produced a mean of 62% with a relative standard deviation of 5% (for four replications) at pH 6.0.

*Reagents*

All chemicals were of reagent grade and were used without further purification except for concentrated nitric acid which was distilled once from all glass-still. Potassium nitrate was recrystallized once from the distilled nitric acid of 4M. Analar grade  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{Pb}(\text{NO}_3)_2$  salts were used to prepare 1000 ppm Cu(II) and 1000 ppm Pb(II) respectively in deionized distilled water.

**RESULTS***Effect of pH*

*Fig. 1* represents the amount of copper (II) taken up by the waste beverage as a function of pH. The degree of uptake increases as pH increases as shown by the decreasing amount of Cu in solution with changes in pH. The optimum pH range for maximum metal uptake appear to

lie between 5 to 7 and 6 to 9 for wastes tea leaves and coffee powder respectively. Hence, in all the other studies, a pH of about 6 was employed.

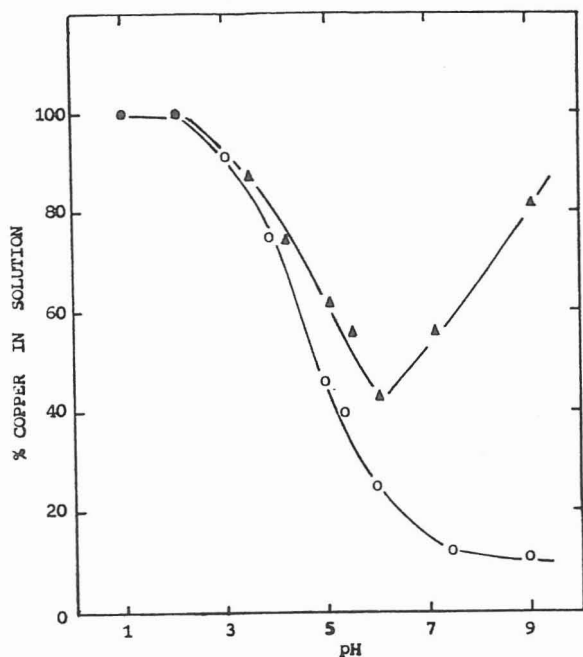


Fig. 1. Copper uptake as a function of pH. 30 mg beverage waste:  $\blacktriangle$  tea,  $\bullet$  coffee,  $[Cu]_{initial} = 2ppm$  in 50 ml solution

It was observed that the metal uptake decreased at the more alkaline condition for tea but not for coffee substrates. At pH > 7, the tea sample solution which was originally colourless turned brownish orange. The solution became more brownish orange as it became more alkaline indicating denaturalization of some cell wall constituents. This denaturalization may have caused the reduction of interacting sites and hence reduce Cu(II) uptake by the tea waste.

Effect of Metal Ion Concentration

Fig. 2 shows that as the concentration of copper ion introduced to the fixed quantity of tea or coffee waste at weakly acidic conditions was increased, a sharp increase in the uptake of copper was seen until a certain concentration was reached, above which the slope levelled off. These two concentration dependent curves assume a Langmuir Isotherm.

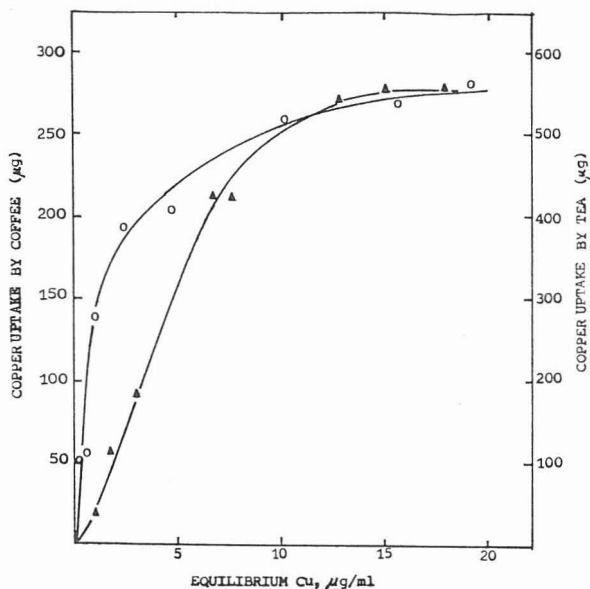


Fig. 2. Copper intake isotherms at pH 6.0 in 50 ml solutions containing:  $\blacktriangle$  20 mg tea waste  $\bullet$  10 mg coffee waste

Nature of the Substrate

Metal uptake by the increasing concentration of the beverage substrate was approximately linear below 10 mg substrate for both the tea and coffee.

A rather small difference in the metal uptake capacity of 3% was seen between the activated (oven heating at 112°C for 4 hours) and the non-activated beverage wastes (air drying) as shown in Table 2. Table 2 also indicates that the effect of grain size of coffee on the metal

TABLE 2  
Physical effect of wastes on the uptake of copper; pH 6, 30 mg beverage,  $(Cu)_{initial} = 4.1$  ppm in 50 ml solution

	% copper uptake by		
	tea	coffee	
		(fine)	(coarse)
Activated	74	82	—
Non activated	72	81	54

uptake capacity is more drastic: everything being equal, the finely ground coffee powder (80 mesh) was able to remove 27% more metal from the solution than the coarse grained coffee (20 mesh). As a result, the finely ground and air dried coffee waste were used in all the other studies.

*Competitive Effects*

Table 3 demonstrates the progressive decrease in the uptake capacity of both the tea

TABLE 3

Effect of ionic strength on the uptake of copper by the 20 mg beverage wastes at pH 6;  $(Cu^{2+})_{initial} = 2.1$  ppm in 50 ml solution

KNO <sub>3</sub> added (molar)	% copper uptake by	
	coffee	tea
0	76	63
0.002	76	62
0.01	74	61
0.05	69	54
0.1	67	49
0.5	55	44

and coffee wastes on the addition of increasing concentrations of potassium nitrate and hence its increasing ionic strength. This suggests the possibility of uptake of  $K^+$  by wastes and hence the competitive effect between this ion and the other ions in solution.

The competitive effect was further studied between two metal ions which were taken up by the same substrate in the same solution at pH 6. This was done by varying the concentration of Pb(II) ions onto the fixed amount of Cu: 5 ppm Cu in 50 ml solution. The two metal ions concentrations at equilibrium were determined simultaneously by differential pulse polarography. Results are summarized in Fig. 4. It demonstrates an obvious decrease in the uptake of copper by wastes from both beverages in the face of increasing competing metal ions. In the presence of 2 ppm Pb in 50 ml solution, the amount of copper uptake was 49 and 67% of the 5 ppm Cu originally present for 30 mg tea and 30 mg coffee substrates respectively. However, a further addition of ten fold excess of Pb concentration caused a further decrease in the amount of Cu uptake by approximately 10 and 5 fold for tea and coffee respectively. Concentration dependent curve for Pb was found to be of the Langmuir type.

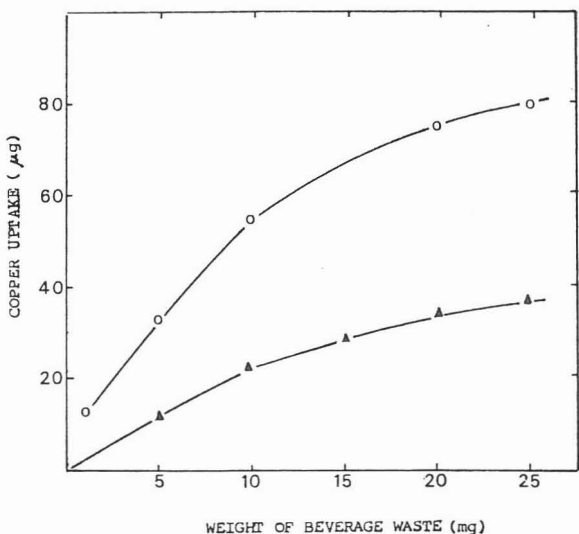


Fig. 3. Copper uptake at pH 6 as a function of the dry weight of  $\blacktriangle$  tea waste;  $\circ$  coffee waste,  $[Cu]_{initial} = 100$   $\mu$ g.

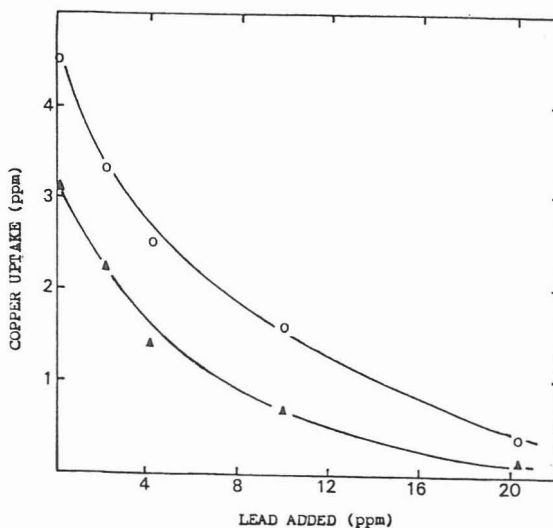


Fig. 4. Effect of added Pb on copper uptake by  $\blacktriangle$  30 mg tea waste;  $\circ$  30 mg coffee waste at pH 5.9,  $[Cu]_{initial} = 5$  ppm

A qualitative experiment involving Triton  $\times 100$ , a strong surfactant was carried out to determine the competitive adsorption effect it had on the observed Cu uptake. Addition of up to 0.0003% Triton- $\times 100$  produced no change in the Cu uptake by the beverage wastes. An obvious change was observed at Triton- $\times 100$  concentration greater than 0.0005% (V/V). An addition of 0.0020% surfactant to both tea and coffee wastes suppressed copper uptake by almost an equal magnitude ( $10 \pm 1\%$ ).

## DISCUSSION

These studies have shown conclusive evidence that the tea leaves and coffee wastes are able to remove metal ions such as Cu(II) from solution. The extent of removal is a function of pH, ionic strength, metal ion concentration, nature of waste substrate used and presence of other competing ions or molecules.

That such uptake of metal is due basically to an adsorption process was qualitatively proven by Triton- $\times 100$  studies. Being a strong surfactant, Triton- $\times 100$  has been commonly accepted as a strong adsorbate. The reduction of metal uptake by the wastes in its presence could only be explained by blocking of their interacting sites by the surfactant which is preferentially adsorbed onto the substrate. These observations are consistent with a mechanism in which adsorption is responsible for the uptake of metal by the beverages.

The actual mechanism involved in the adsorption process of metal by the wastes cannot be easily determined. However studies on the factors governing metal uptake as mentioned earlier revealed results which are consistent with specific adsorption via chelation and some degree of ion exchange reaction.

To illustrate chelation, we consider the equilibria between the polyphenol, which make up almost one-third of the total dry matter in tea (Harler 1963), and other ions present as shown in Fig. 5.

When pH is greater than 3, the interacting sites can dissociate to form negatively charged surfaces which can interact with metal ions in two possible ways:

- i. formation of a counter ion layer,
- ii. specific adsorption of ions onto the surface via chelation as shown in Fig. (5).

Based on this model, the various phenomena of metal adsorption by the beverage wastes can be readily explained. In the presence of proton,  $\text{Cu}^{2+}$  has to compete with it for interacting or chelation sites of the substrate. Hence the more acidic the medium the lesser the chance for  $\text{Cu}^{2+}$  to interact with the adsorbent, which results in decreased metal uptake. On the contrary, as pH increases,  $\text{Cu}^{2+}$  faces lesser degree of competition from  $\text{H}^+$  for the interacting sites. This competitive effect does explain why there was no detectable copper uptake at  $\text{pH} \leq 2$  and greater copper intake as pH increased (Fig. 1).

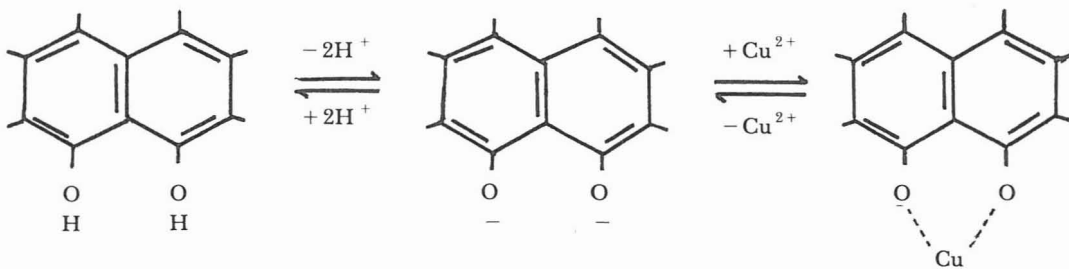


Fig. 5. Interaction of Cu(II) and  $\text{H}^+$  ions with polyphenol groups of beverage wastes.

TABLE 4

Affinity of Cu - Pb couple in 50 ml solution containing 30 mg beverage wastes at pH 5.6

	(M <sup>2+</sup> ) uptake/ppm	% M <sup>2+</sup> uptake
I(a) 5.0 ppm Cu + tea waste	(Cu) : 1.9	38
(a) + 5.0 ppm Pb spike	(Cu) : 1.2	24
	(Pb) : 3.8	76
II (b) 5.0 ppm Cu + coffee waste	(Cu) : 3.4	68
(b) + 5.0 ppm Pb spike	(Cu) : 3.1	62
	(Pb) : 4.0	80
III (5.8 ppm Cu + 3.5 ppm Pb) + tea waste	(Cu) : 1.4	24
	(Pb) : 2.6	74

Competitive effect is not only exerted by H<sup>+</sup> but also other ions like Pb<sup>2+</sup> as shown in Fig. 4 and Table 4. Lead ion appears to have a greater affinity for the surface of the waste than Cu<sup>2+</sup>. It can be demonstrated by the results in Table 4, which show greater adsorption of Pb<sup>2+</sup> over that of Cu<sup>2+</sup> irrespective of the fact that the waste was added to the solution already containing both metal ions or only one metal ion. There was some indication that the interactions of Cu - Pb couple with the wastes involved small but significant degree of ion-exchange reaction. This is because about 6 to 14% Cu adsorbed was released into the solution after the addition of Pb to the mixture (Table 4 (I), (II)).

The increasing suppression of metal uptake by beverage waste due to increasing ionic strength of the sample solutions at pH 6.0 can be attributed to the formation of a counter ion layer by K<sup>+</sup> ions. These K<sup>+</sup> layers would invariably act as a deterrent for the specific adsorption of copper. In general, K<sup>+</sup> appears to have a smaller affinity for the beverage substrate as compared to that of Cu<sup>2+</sup> and Pb<sup>2+</sup>. An addition of as much as 0.5M KNO<sub>3</sub> does not cause any drastic decrease in the copper adsorption by the waste. This occurs because the potassium ion is monovalent while copper and lead ions are divalent.

The studies carried out so far concern mainly the copper uptake by tea and coffee wastes using a batch technique. Research is now in progress to investigate the adsorption behaviour of other metals such as zinc, cadmium and lead.

Similar studies shall also be extended to column technique and optimum parameters such as pH, flow rate, etc. shall be determined for the removal of metals from some wastewaters.

#### ACKNOWLEDGEMENTS

This work was supported by a Universiti Pertanian Malaysia Research Grant and has been presented at the 1984 International Chemical Congress of Pasific Basin Societies, Honolulu, Hawaii. The author also wishes to thank Dr. M. Shamin for reviewing the draft copy and laboratory staff, Talib Ali and C.S. Choo, for their technical assistances and Noraini bt Abu Bakar for the typing of the manuscript.

#### REFERENCES

- CHANEY, R.L. and HUNDEMANN, P.J. (1979): *J. Water Pollution Control Federation*. 51: 17.
- FARRAH, H. and PICKERING, W.F. (1976): *Aust. J. Chem.* 29: 1167.
- FARRAH, H. and PICKERING, W.F. (1976): *Aust. J. Chem.* 30: 1417.
- GUY, R.D., CHAKRABARTI, C.L. and SCHRAMM, L.L. (1975): *Can. J. Chem.* 53: 661.
- HARLER, C.R. (1963): 'Tea Manufacture' p. 108. New York. Oxford Univ. Press.
- HUANG, C.P., ELLIOTT, H.A. and ASHMEAD, R.M. (1977): *J. Water Pollution Control Federation*. 49: 745.
- KNOCKE, W.R. and HEMPHILL, L.H. (1981): *Water Research*. 15: 275.

- MOORE, J.J. and MOORE, E.A. (1976): *Environmental Chemistry*. p. 318. New York. Academic Press, Inc.
- NETZER, A., WILKINSON, P. and BESZEDITS, S. (1974): *Water Research*. **8**: 813.
- POSSELT, H.S., ANDERSON, F.J. and WEBER, W.J. Jr. (1968): *Environ. Sci. Technol.* **2**: 1087.
- RANDALL, J.M. (1974): *Forest Product Jour.* **24**: 81.
- SIVETZ, M.S. (1963): '*Coffee Processing Technology*' Vol. 2, p. 167. Connecticut. The Avi Publishing Company, Inc.

(Received 7 January, 1985)