Paraquat Adsorption Characteristics of Some Malaysian Soils

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ABSTRACT

This adsorption study showed that adsorption of paraquat varied between the soil samples studied. The adsorption was related to the organic matter content of the samples. However, the inorganic components of the soil also contributed to the adsorption. Hence, both the inorganic and organic components of the soils were involved in the paraquat adsorption. The adsorption followed both the Langmuir and Freundlich adsorption isotherms.

INTRODUCTION

1, 1'-dimethyl 4, 4'-bipyridylidium ion, commonly known as paraquat, is available commercially as dichloride salt and is a widely used herbicide in Malaysia. In aqueous solution, this pesticide exists as divalent cations with their positive charges distributed around the molecules (Hayes et al., 1975; Buidon et al., 1977).

Interaction, particularly adsorption, of a pesticide with soil is an important factor affecting the fate of pesticides in the soil environment, and the organocation paraquat is no exception. Adsorption will control the quantity of the pesticide in soil solution and thus determine its persistence, mobility and bioavailability. The extent of adsorption depends on the chemical nature of the soil environment.

Adsorption of paraquat by soil is related to soil components. The clay and organic components have a major contribution towards the adsorption (Knight and Tomlinson, 1967). The role of organic matter in the soil is quite significant. Paraquat is known to become inactivated in high organic soils (Khan et al., 1976; Damanakis et al., 1970; Calderbank, 1968). Reviews by Burns and Hayes (1974) and Khan (1974), stated that humic substances have a high affinity for paraquat. The adsorption is however influenced by the resident inorganic charge balancing cations in the humic polymer.

Specific studies showed that clay minerals also have a high affinity for paraquat (Haque et al., 1970; Hayes et al., 1975). Adsorption affinity is in the order vermiculite > montmorillonite > illite > kaolinite (Hayes et al., 1975). The oxide component also contribute towards paraquat adsorption in soil (Oladimeji, 1976).

This paper describes some paraquat adsorption characteristics of six Malaysian soils, with particular emphasis on the contribution of the organic and inorganic components of the soils towards the adsorption.
MATERIALS AND METHODS

Six Malaysian soil samples were used in this study and the source of each soil is given in Table 1. Only the < 1mm fraction of the air-dried soil samples were used in the chemical and adsorption analyses.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>Danum Valley rainforest</td>
</tr>
<tr>
<td>S2</td>
<td>Forest plantation</td>
</tr>
<tr>
<td>S3</td>
<td>Secondary forest</td>
</tr>
<tr>
<td>S4</td>
<td>Tin mining area</td>
</tr>
<tr>
<td>S5</td>
<td>Mangrove swamp</td>
</tr>
<tr>
<td>S6</td>
<td>Podzol (B horizon)</td>
</tr>
</tbody>
</table>

The pH of each soil sample was measured in a 1:2 suspension using distilled water. Organic carbon content was determined by the Walkley-Black method (1934), while the cation exchange capacity was determined by the ammonium acetate method (Chapman, 1965).

For the adsorption studies, 2g of soil sample was equilibrated for 12 hours with 25ml of paraquat solution with concentrations ranging from 5.52 - 27.56mg/ml. The paraquat solutions were prepared from paraquat dichloride (ICI Malaysia Ltd). After equilibration, the paraquat solution was separated from the soil residue by centrifugation and then filtration. The absorbance of the aliquot was determined at 640nm in a UV spectrophotometer. The absorbance values for paraquat solutions of known concentrations were also determined in order to obtain a calibration curve. The final solution concentrations of the added paraquat were determined from the calibration curve. The difference between the initial and final concentrations gave the amount of paraquat adsorbed. The same procedure was used with S5 and S6 samples pretreated to remove the organic matter by heating at 550°C for 5 hours. The treated samples were designated S5-Tr and S6-Tr, respectively. Ignition of soil at high temperature can cause destruction of organic matter (Nelson and Sommers, 1982), and in fact has been used to estimate soil organic matter (Davies, 1974).

RESULTS AND DISCUSSIONS

Table 2 shows some chemical properties of the soil samples. Basically the soils varied in pH, organic carbon content and cation exchange capacity (CEC). Organic carbon or organic matter content was highest in the mangrove soil sample (S5) while the lowest value was found in the soil sample from a tin mining area (S4). The organic carbon contents of the treated S5 and S6 samples were not determined. However, since the ignition process is capable of destroying soil organic matter (Nelson and Sommers, 1982) they should differ significantly from the original samples in organic carbon content. The cation exchange capacities of the soils were poorly correlated ($r = 0.7599$) to their organic matter contents. This indicated that other components present in the soil also contributed to the CEC of the soils.

The calibration curve of paraquat is shown in Figure 1. Within the concentration range studied, the absorbance values were directly proportional to concentrations.

The paraquat adsorption data and isotherms are shown in Table 3 and Figure 2 respectively. Five levels of paraquat were added to
Paraquat adsorption characteristics of some Malaysian soils

The soils and the amount adsorbed varied between samples. The amount adsorbed also depended on the initial concentration of paraquat. For each level of paraquat addition, the amount adsorbed was in the order $S_5 > S_6 > S_1 > S_3 > S_4 > S_2$, and was least in samples with low organic matter content. Comparison of untreated and treated $S_5$ and $S_6$ samples is given in Figure 3. The treated samples showed a significant reduction ($>50\%$) in the amount of paraquat adsorbed. This suggests that the organic matter component of the soils contributed considerably to paraquat adsorption. Similar adsorption characteristics following organic matter removal by hydrogen peroxide and sodium hypochlorite have been obtained by Knight and Tomlinson (1967) and Oladimeji (1976) respectively. Organic matter or humic substances are known to have a high affinity for paraquat (Burns and Hayes, 1974; Khan, 1974; Khan, 1973; Burns et al., 1973). This is mainly due to the presence of functional groups like $-\text{COOH}$ and $-\text{OH}$. The paraquat cation can react with more than one of these functional groups (Stevenson, 1976). The mechanism of adsorption is predominantly ion exchange (Burns et al., 1973; Best et al., 1977; Schnitzer and Khan, 1972).

The treated $S_5$ and $S_6$ samples were still capable of adsorbing $4-6\%$ of the added paraquat concentration.

\begin{table}[h]
\centering
\caption{Paraquat adsorption data for the soil samples}
\begin{tabular}{lcccccccc}
\hline
Paraquat added (mg g$^{-1}$) & Paraquat adsorbed (mg g$^{-1}$) \\
& S1 & S2 & S3 & S4 & S5 & S5-Tr & S6 & S6-Tr \\
\hline
69 & 21.9 & 1.1 & 19.9 & 3.9 & 52.5 & 3.9 & 43.8 & 3.0 \\
138 & 28.7 & 1.9 & 22.6 & 6.3 & 82.0 & 6.2 & 45.1 & 5.6 \\
207 & 38.7 & 3.0 & 24.6 & 9.3 & 118.7 & 8.7 & 46.7 & 8.4 \\
276 & 40.0 & 5.3 & 25.5 & 12.3 & 149.0 & 11.2 & 51.2 & 10.9 \\
345 & 46.7 & 6.7 & 27.7 & 14.5 & 153.7 & 13.8 & 57.0 & 11.3 \\
\hline
\end{tabular}
\end{table}
quat. The removal of organic matter from the soils would normally leave behind the more resistant inorganic component of the soil. This component, therefore, most likely gave a major contribution to paraquat adsorption on the treated samples. The studies by Knight and Tomlinson (1967) and Oladimeji (1976) also showed that paraquat was still adsorbed after removal of the organic component. The amount of paraquat adsorbed by the treated S5 and S6 samples were comparable to the amount adsorbed by sample S4 which had the least organic matter. These results showed that both the organic and inorganic components in the soil contributed to the paraquat adsorption.

The paraquat adsorption on the soil samples followed both the Langmuir (except S2) and Freundlich adsorption isotherms. The respective correlation coefficients are given in Table 4. The values of the adsorption maxima, that is the maximum amount of paraquat that can be adsorbed on the soil samples, were

**Table 4**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td>S2</td>
<td>0.55 ns</td>
<td>0.95</td>
</tr>
<tr>
<td>S3</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td>S4</td>
<td>0.87</td>
<td>0.99</td>
</tr>
<tr>
<td>S5</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td>S5-Tr</td>
<td>0.88</td>
<td>0.99</td>
</tr>
<tr>
<td>S6</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td>S6-Tr</td>
<td>0.88</td>
<td>0.99</td>
</tr>
</tbody>
</table>

\(^4{p < 0.001}; \quad ^5{p > 0.001}; \quad ^2{p > 0.05}; \quad ^1{p > 0.01}\)
calculated from the Langmuir isotherms. The relationship between the adsorption maximum and the organic carbon content of the soil samples is shown in Figure 4. There was a good linear relationship (r = 0.9111) between the two parameters. Such relationship indicated that organic matter played an important role in the paraquat adsorption. There was a positive correlation (r = 0.8059) between the adsorption maximum and the cation exchange capacity (Figure 5). This was an indication of the possibility of ion exchange mechanism for the paraquat adsorption.

CONCLUSION
This study indicates that the amount of paraquat adsorbed by the Malaysian soils studied varies between samples. The inorganic component and particularly the organic component in the soil samples contribute towards the adsorption, and the adsorption generally follow both the Langmuir and Freundlich adsorption isotherms.

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REFERENCES

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