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In Vitro Adsorption Characteristics of Paraquat and Diquat with Activated Carbon Varying in Particle Size

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Paraquat and diquat are non-hormone, non-selective herbicides. They are used all over the world because of their superior herbicidal effect. It was reported that herbicides were unlikely to give rise to serious health problems when properly used (Swan 1969, Howard 1980). After the report of two cases of death by ingestion of paraquat in 1966 (Bullivant 1966), however, the instances of acute poisoning increased and became a social problem in Japan (Ukai & Kawase 1985). The production of highly concentrated paraquat (24%) was discontinued at 1986. Now the mixed preparation (paraquat 5%, diquat 7%) is on the market.

The effective therapy for acute paraquat and/or diquat poisoning has not been established. The fundamental cure of paraquat and diquat poisoning is the selective excretion of toxic substances out of body by means of gastrointeistinal lavage. and the administration of adsorbents and purgatives. Among adsorbents, activated carbon has been evaluated as a reliable, safe and inexpensive antidote and is recommended for use in the treatment of acute poisoning (Neuvonen 1982, Neuvonen & Olkkola 1988,Palatnick & Tenenbein 1992). However,one of the major problems in handling of activated carbon at the emergency site is the scattering of fine particles. Therefore, in this investigation we studied the in vitro adsorption characteristics of paraquat and diquat by different particle sizes of activated carbon.

MATERIALS AND METHODS

The mixed preparations of paraquat and diquat (Pregrox L) in the adsorption experiments was obtained from Nihon Noyaku Co. Ltd. The standard solutions for calibration curves were prepared by using paraquat and diquat for the test of agricultural chemical residue (Wako Pure Chem Co. Ltd.). Activated carbon was obtained from Takeda Chem. Ind. Ltd. Shirasagi G. The activated carbon was ground to smaller particles, and

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sieved to several particle sizes. The particle sizes of activated carbon were ranged 10-20, 20-32, 32-48 and 48-80 mesh, respectively. Before use, activated carbon was washed in distilled and deionized water. Then it was dried 110 °C for 48 hours, and kept in a desiccator. The surface area and the pore volume of activated carbons were measured using a BET apparatus with nitrogen gas at liquid nitrogen temperature (Brunauer *et al* 1938).

The adsorption isotherms of paraquat and diquat onto activated carbon were measured as followed: Five hundred milligrams of activated carbon was shaken with 50 mL of the solution with different concentrations of mixed preparations by dilution for 48 hours at 37°C . After filtration, unadsorbed paraquat and diquat concentrations in the filtrate were measured at 255 and 310 nm with a spectrophotometer (Shimadzu, UV-1200) (Yuen *et al* 1967). The amounts of paraquat and diquat adsorbed was calculated from the difference between the initial total amount and the amount of unadsorbed.

The time courses of removal ratio were measured in the diluted solution of mixed preparations / activated carbon system at 37°C . Five grams of activated carbon was added to a stirred diluted solution of the mixed preparations of 200 mL (300 rpm). One milliliter of the suspension was taken up at regular intervals and then the paraquat and diquat concentration was measured by spectrophotometry.

RESULTS AND DISCUSSION

The properties of activated carbons were indicated in Table 1. Even if the particle size of activated carbon is more smaller, a marked difference in properties was not recognized.

Table 1 Physical Properties of Activated Carbons.

particle size (mesh)	specific surface area (m^2/g)	pore volume (mL/g)
10-20	1113	0.655
20-32	1120	0.628
32-48	1124	0.620
48-80	1129	0.611

Adsorption isotherms of paraquat and diquat onto activated carbons applied to the Freundlich equation (Hassler 1963) and then the equilibrium amount adsorbed at each concentration was calculated. The

Freundlich equation can be expressed in the following form,
$\text{Log } V = 1/n \text{ Log } C + \text{Log } k$,
where V is the amount adsorbed per unit mass of adsorbent, C is the equilibrium concentration, and n and k are the experimental parameters which depend on system of adsorbent and adsorbate. The k is an empirical constant equal to the intercept at C = 1 mg/L and l/n is the slope of the line on a log-log plot. Tables 2 and 3 indicated the equilibrium amounts of paraquat and diquat adsorbed at each concentration, respectively. There was no difference in the amount adsorbed onto activated carbon different in particle size (Tables 2 and 3).

Table 2 Equilibrium amount of paraquat adsorbed onto activated carbons.

Particle size (mesh)	Amount of paraquat adsorbed (mg/g)		
	1 mg/L	10 mg/L	100 mg/L
10-20	7.05	15.14	32.49
20-32	6.50	14.65	33.04
32-48	4.71	11.92	30.15
48-80	6.00	14.07	32.98

Table 3 Equilibrium amount of diquat adsorbed onto activated carbons.

Particle size (mesh)	Amount of diquat adsorbed (mg/g)		
	1 mg/L	10 mg/L	100 mg/L
10-20	4.99	9.26	17.19
20-32	7.31	11.29	17.44
32-48	6.88	10.97	17.49
48-80	4.41	9.02	18.42

In general, adsorption capacity of activated carbon is dominated by surface area and pore volume (Giusti *et al* 1974, Puri *et al* 1976). The fact that there is no difference in the equilibrium amounts adsorbed onto activated carbon of different particle sizes can be explained by the properties of activated carbon indicated (Table 1).

The equilibrium amount of paraquat adsorbed was greater than that of diquat. Activated carbon adsorbs non-polar substances in general. The one-electron reduced potential of paraquat and diquat is -0.43V and -0.36V, respectively. That is, diquat is liable to receive an electron than paraquat. In other words, the polarity of diquat is stronger than that of paraquat (Nakasa *et al* 1990). Therefore, it is assumed that the difference in the amount adsorbed between paraquat and diquat onto activated carbon is due to the difference in strength of polarity of paraquat and diquat.

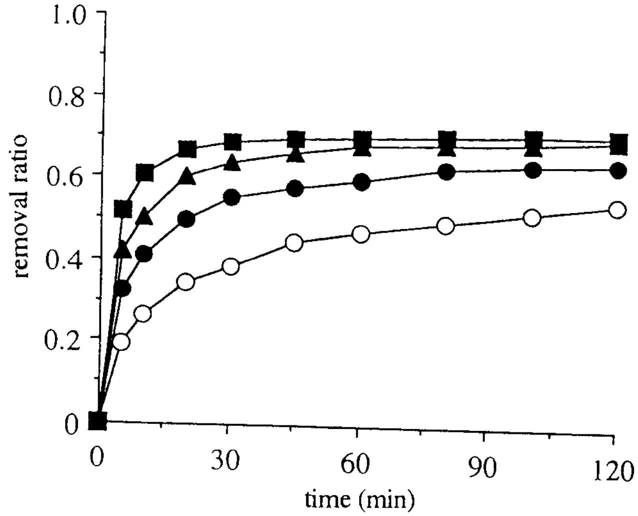

Figure 1. Time courses of removal ratio of paraquat by activated carbon at 37℃.
particle size (mesh):○:10-20,●:20-32,▲:32-48,■:48-80.

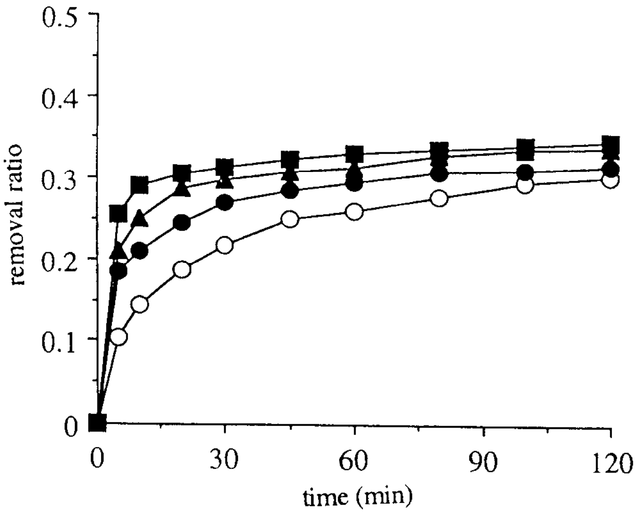

Figure 2. Time courses of removal ratio of diquat by activated carbon at 37℃.
particle size (mesh):○:10-20,●:20-32,▲:32-48,■:48-80.

In the evaluation of adsorbent, the removal rate is another factor to be determined. The time courses of removal ratio of paraquat and diquat were shown in Figures 1 and 2, respectively. Removal ratio was calculated according to the following formula,

Removal ratio = $(C_0, - Ct) / C_0$,

where C_0 is the initial concentration and Ct is the concentration at each elapsed time. For both paraquat and diquat, the smaller the particle size of activated carbon, the faster toxic substances were removed (Figs. 1 and 2). The smaller the particle size of activated carbon. the larger the contact surface area to adsorbate. Therefore, it is assumed that the increase of contact surface area accelerated the removal of paraquat and diquat onto activated carbons.

At the emergency site, the rapid removal of toxic substances from the gastrointestinal tract is important. In the removal of toxic substances with adsorbents, the particle size is thought to be an important factor in the removal characteristics of toxic substances.

In the use of activated carbon as an oral adsorbent for the emergency treatment of acute paraquat and diquat poisoning, it is suggested that paraquat and diquat is removed more rapidly by using of activated carbon with smaller particle size. However, the selection of suitable activated carbon still stand discussion from the handling.

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