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Kinetics of *in vitro* Paraquat Removal by Cation-Exchange Resin

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Paraquat(1,1'-dimethyl-4,4'-dipyridylium salt) has been extensively used as a herbicide because of its superior herbicidal effect. In general use, it has no poisonous effect (Swan 1971). In recent years, however, instances of poisoning due to its misapplication or ingestion for suicide have increased. The rate of its use for the latter purpose is higher than that of any other agricultural chemical, and an effective antidote and treatment for paraquat poisoning have not been found. Presently, treatment involves removal of paraquat remaining in the digestive tract and that already been adsorbed. For example, gastrointestinal lavage, administration of cathartic and adsorbents, forced diuresis, and direct hemoperfusion are carried out as primary treatment.

For use as adsorbents, the efficacies of Fuller's earth, bentonite, aluminum silicate, and activated carbon have been reported(Clark 1971, Okonek et al 1982) as well as those of cation-exchange resins (Staiff et al 1973, Nokata et al 1984). So far, little attention has been directed to adsorbents for treating paraquat poisoning in vitro. In the present study cation-exchange resins were examined as adsorbents for paraquat removal and their characteristics in terms of removal capacity and kinetics were investigated.

MATERIALS AND METHODS

Paraquat was obtained as a commercial preparation (Gramoxone S, Nihon Nohyaku Co., Ltd.) and its concentration was indicated as 24%. Cation-exchange resin was purchased from a commercial source.

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The adsorption capacity of the cation-exchange resin was determined _in vitro_. Five hundred milligrams of adsorbent were shaken with 50mL of paraquat solution previously diluted with artificial gastric juice(Ca. 800mg/L) at a constant temperature of 37°C for 24 hrs. After extraction using a Sep-Pak C18 cartridge as the filtrate(Tsunoda 1983), the paraquat concentration was measured photochemically by the method of Calderbank and Yuen (1965).

The adsorption rate of the paraquat-artificial gastric juice / adsorbent system was measured at 37°C. Five grams of adsorbent were introduced into a stirred solution of one liter of paraquat solution(Ca.800mg/L). Five milliliters of the suspension were taken up at regular intervals followed by measurement of the paraquat concentration.

RESULTS AND DISCUSSION

The removal ratios by cation-exchange resin and activated carbon are shown in Table 1, the former being about 2.5 times that of the latter. It is thus evident that the exchange resin more effectively removes the paraquat than the activated carbon.
That is, ion exchange action is more effective than pore adsorption for paraquat removal. No significant correlation was found between the removal ratio and properties of the cation-exchange resin. Neither was significant variation found in the pH of the solution before and after administration of the adsorbent, as Table 1.

Table 1. Removal Ratio of Paraquat by Activated Carbon and Cation-Exchange Resin, and Final pH in Solution.

No.	adsorbent	removal ratio (%)	final pH
1	activated carbon	32.80	1.49
2	activated carbon	39.92	1.50
3	amberlite	91.43	1.49
4	amberlite	82.45	1.58
5	amberlite	98.57	1.50
6	amberlite	88.44	1.49
7	kayexalate	98.55	1.51

Initial conditions: Co;781.35 mg/L, pH;1.52

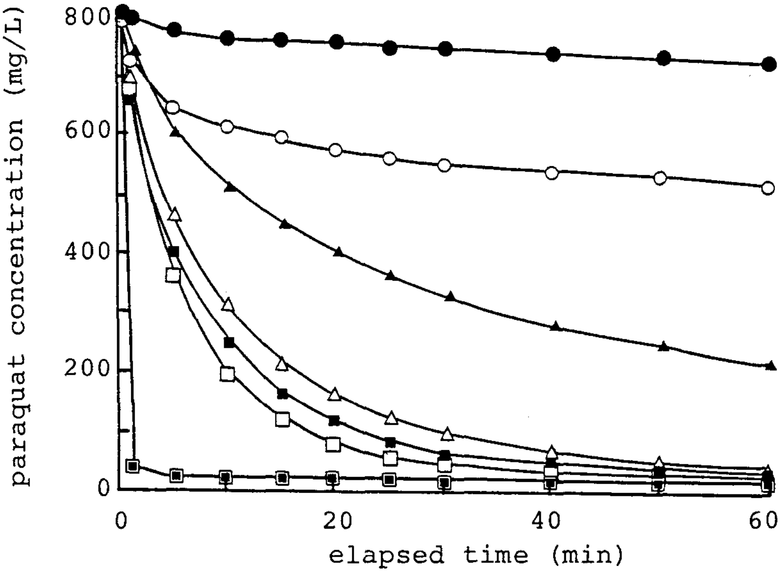

Figure 1. Variation of Paraquat Concentration with Elapsed Time. ●:No.1, ○:No.2, ▲:No.3, △:No.4, ■:No.5, □:No.6, ▣:No.7.

Figure 1 shows variation in paraquat concentration with time. The use of Kayexalate caused the concentration to lower remarkably and after 5 minutes, it reached a plateau. After 60 minutes, it was 508.29-727.67mg/L in activated carbon, and 27.03-214.09mg/L in the cation-exchange resin. Kinetic constants(k) were calculated to elucidate adsorption rates according to the equation,

$$\log C0/Ct = kt$$

where C0 is the initial concentration and Ct, the concentration at time t. Calculations were made using data for 30 minutes since linearity reliability 30 minutes exceeded that for 60 minutes. Table 2 shows kinetic constants obtained by the cation-exchange resin. These values were found correlated to the properties of the resin. This indicates that there is a significant correlation between the kinetic constants and the degree of crosslinkage (divinylbenzene contents), as shown in Figure 2. It may thus be concluded that the adsorption rate of paraquat by the cation-exchange resin is determined primarily by the number of its crosslinkages.

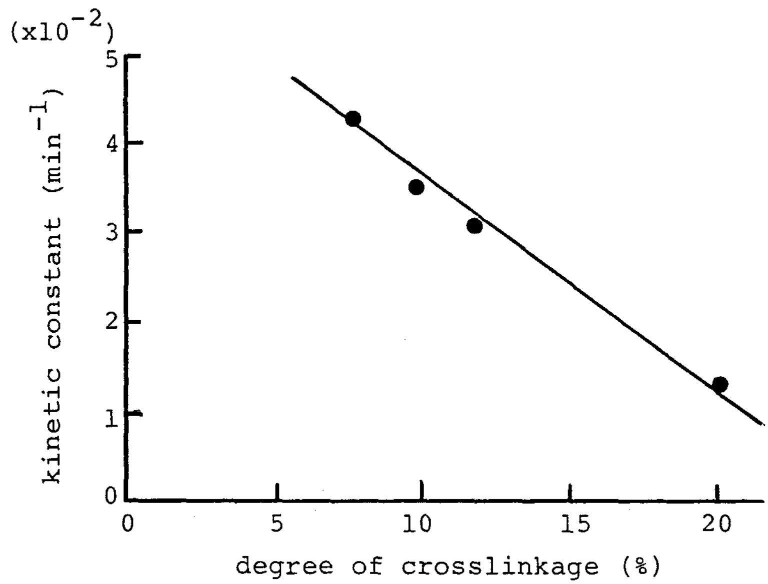

Figure 2. Correlation of Kinetic Constant with Degree of Crosslinkage of Cation-Exchange Resin.

Table 2. Kinetic Constants by Cation-Exchange Resin.

No.	kinetic constant (min^{-1})
3	0.0126
4	0.0308
5	0.0350
6	0.0422

In recent years, cation-exchange resin has been used for treating paraquat poisoning and its effects have been examined(Nokata _et al_ 1984). However, nothing has been said regarding adsorption by the resin. Fujita and Okazaki(1987) reported cation-exchange resins with sulfonic acid groups to show the highest adsorption for urea, the amount adsorbed being directly proportional to the degree of ion exchange. In this study, in spite of the participation of the sulfonic acid group of the resin in adsorbing the paraquat, no significant correlation was not found between the adsorption ratio and degree of ion exchange. The adsorption rate was affected by the degree of crosslinkage in the resin. The adsorption rate in the case of gel-type resins may possibly be faster than that in the case of macro-reticular type resins.

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