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Acceleration of Paraquat Adsorption onto Chitosan by the Presence of Sodium Chloride

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Paraquat has been widely used as a superior herbicide and is unlikely to produce serious problems when properly used (Swan 1969, Howard 1980). In Japan, however, many people have died through accidental, suicidal or homicidal ingestion of paraquat. The mortality from paraquat poisoning is higher than that from any other type of poisoning associated with agricultural chemicals (Ukai and Kawase 1985). Although the production of paraquat preparations of high concentration (24%) has been discontinued in July 1986 in Japan, the mixture preparation (paraquat 5%, diquat 7%) is on the market as "Pregrox" today. The LD_{50} (oral) of paraquat for man is assumed to be 40mg/kg (Natori 1979).

One of the first steps in the treatment of acute poisoning is the removal of poison from the digestive tract. Gastric lavage, irrigation of the colon, administration of adsorbents and/or purgatives, forced diuresis, hemoperfusion and so on are performed for removing paraquat. In primary therapy for acute paraquat poisoning, adsorbents are administered orally (Okonek *et al.* 1982-83; Smith *et al.* 1974; Nokata *et al.* 1984). At present, no specific and effective antidote for paraquat poisoning is available.

Chitin, β-(1-4)-poly-N-acetyl-D-glucosamine, and chitosan, deacetylated chitin have recently drawn great interest from the standpoint of utilization of natural resources (McKay *et al.* 1983; Yoshida *et al.* 1991). Chitin and chitosan may be useful as antidites because they are low in toxicity, biocompatible, and biodegradeable. However, little studies on the evaluation of chitosan as a paraquat adsorbent have been done so far (Tanada *et al.* 1991).

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In this investigation, we discuss the acceleration of paraquat adsorption onto chitosan by the presence of sodium chloride.

MATERIALS AND METHODS

Paraquat was obtained from Wako Pure Chem. Co. Ltd. and used as the test chemical. Four chitosan products BCW2510 (CH-1), BCW 2610 (CH-2), BCW 3010(CH-3) and BCW 3510 (CH-4), obtained from Fuji Spinning Co. Ltd., were used. The particle sizes of these products ranged from 0.9-1.0 mm.

The adsorption capacity of paraquat by chitosan was evaluated *in vitro*. One gram of chitosan was added to 200 ml of a stirred paraquat solution (*ca.* 20 mg/l) at 37 ℃, and the paraquat concentration in the suspension were measured by a colorimetric method with an alkaline sodium dithionite solution at regular intervals (Calderbank and Yuen 1965). Ratios of sodium chloride addition to paraquat solution were 0.9, 1.8 and 2.7 %.

RESULTS AND DISCUSSION

Table 1 shows the physical properties of chitosan. The value of surface area was quoted from technical data of manufacturer and the bulk density was measured by crude packing method. The surface area and bulk density of CH-4 were 1.7 and 1.4 times greater than those of CH-1, respectively.

Table 1. Surface Area and Bulk Density of Chitosan.

	CH-1	CH-2	CH-3	CH-4
surface area (m^2/g)	120.5	131.4	142.3	203.6
bulk density (mg/ml)	82.7	76.4	82.7	112.3

Figure 1 shows the structure of substituents group of C_2-amino group. CH-1, CH-2 and CH-3 have aliphatic substituent groups and CH-4 has aromatic one.

Sodium chloride enhanced the adsorption of paraquat by all four chitosan products tested and adsorption was depended on time, concentration of sodium chloride, and the structure of the chitosan products as shown in Figure 2. The major differences in adsorption appeared to be related to the structure of chitosans tested. The CH-1 is quaternary structure, and the charge is positive in the neutral solutions.

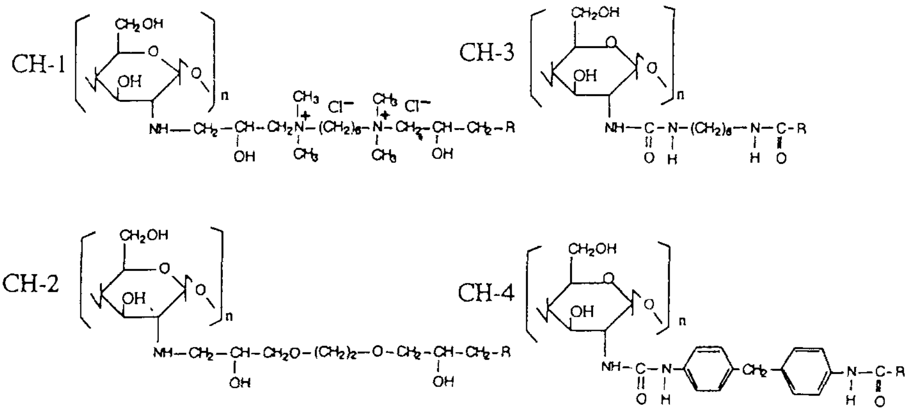

Figure 1. Structure of Substituents Group of C_2-amino Group.

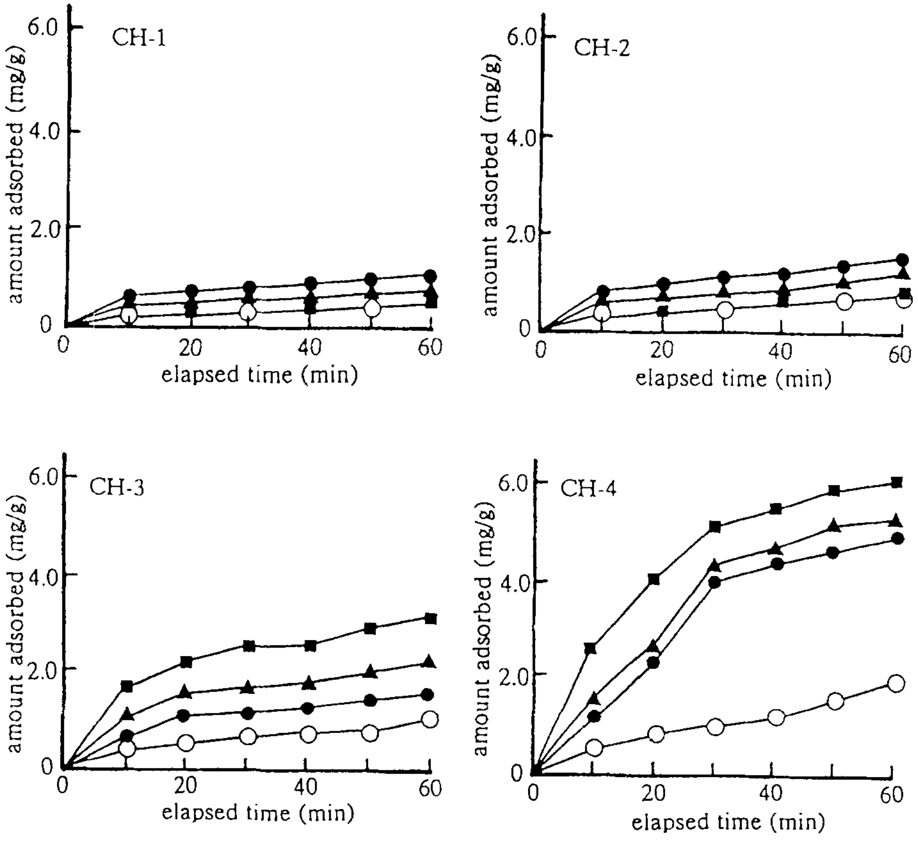

Figure 2. Time Courses of the Amount of Paraquat Adsorbed onto Chitosan.
sodium chloride concentration;○: 0 %,● : 0.9 %,▲: 1.8 %,■ : 2.7 %

Paraquat is dissociated into cation. Therefore, it is considered that a mutual repulsion between the positively charged CH-1 and paraquat cation inhibits the adsorption of paraquat. On the other hand, the CH-3 and CH-4 have two peptide bonds, and these carbonyl groups will be charged negatively. So the adsorption removal of paraquat onto CH-3 and CH-4 is superior to that onto CH-1 due to the electrostatic interaction between the negative charged chitosan and paraquat cation.

The zero-order adsorption rate constants were calculated. Table 2 shows the kinetic constants by chitosan in presence of sodium chloride. The kinetic constants by all chitosan in 0.9% of NaCl were increased. The adsorption rate of paraquat by chitosan was accelerated 1.8-2.9 times in the presence of 0.9% of NaCl. As the sodium chloride concentration was over 0.9%, however, kinetic constants by CH-1 and CH-2 were decreased. Those by CH-3 and CH-4 were increased with the increase of sodium chloride concentration.

Table 2. Kinetic Constants of Paraquat Removal by Chitosan.

	kinetic constant ($\times 10^{-2}$ mg/g.min^{-1})			
NaCl (%)	CH-1	CH-2	CH-3	CH-4
0	0.654	0.904	1.314	3.014
0.9	1.421	2.071	2.457	8.671
1.8	0.896	1.586	3.225	9.211
2.7	0.761	1.054	4.368	9.579

Figure 3 shows the relationship between the amount of paraquat adsorbed after 60 minutes of elapsed time, kinetic constant and sodium chloride concentration. Except for CH-3, both amount adsorbed and kinetic constant by chitosan was nearly great in 0.9% of sodium chloride concentration. It is assumed that the suitable sodium concentration is 0.9% for the removal of paraquat by chitosan.

The enhancing effect of saline purgatives on the *in vitro* adsorption of drugs by activated charcoal has been reported. Ryan *et al.* (1980) reported the effect of magnesium citrate on the ability of activated charcoal to adsorb sodium salicylate. They found that more salicylate was adsorbed onto activated charcoal in the presence of magnesium citrate than in water alone. Lapierre *et al.* (1981) also reported that magnesium citrate actually accelerated the ability of activated charcoal to adsorb aspirin in a simulated intestinal solution.

On the adsorption of paraquat onto activated carbon, it has been reported that the ability is accelerated in a normal saline

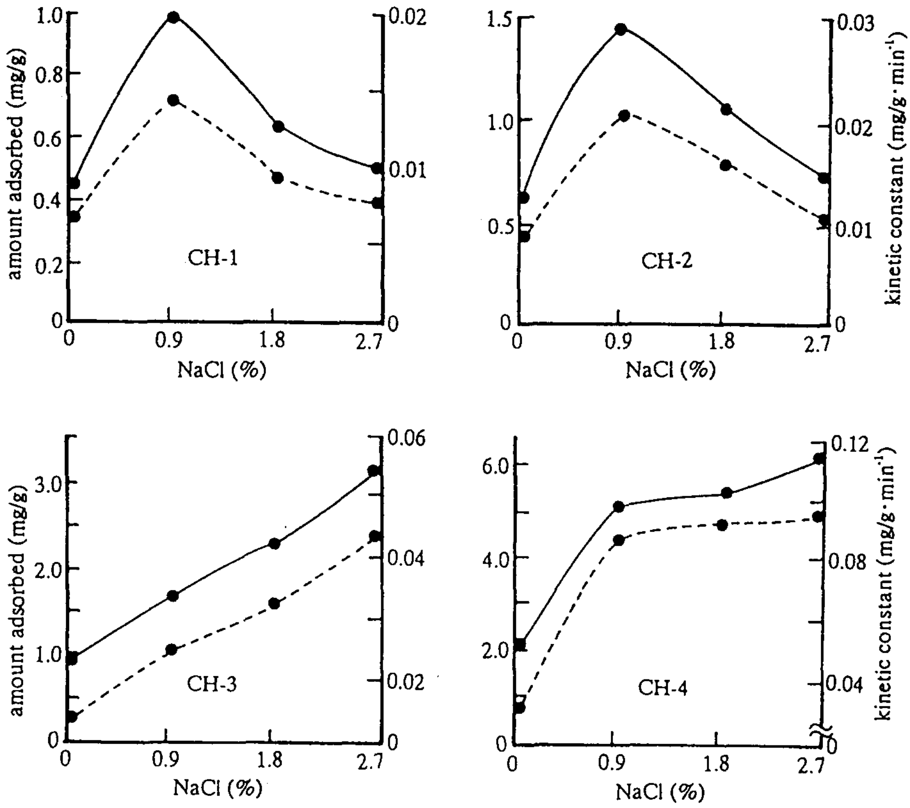

Figure 3. Relationships between the Amount of Paraquat Adsorbed, Kinetic Constant and Sodium Chloride Concentration.
full line, amount adsorbed dotted line, kinetic constant.

solution (Nakamura *et al.* 1989). The presence of sodium chloride accelerated the removal ability of activated carbon for paraquat, but that interfered the ability of cation exchange resin (Kitakouji *et al.* 1989).

In the case of chitosan, the ability for paraquat was accelerated in the presence of sodium chloride. Therefore, it was found that the removal mechanism of chitosan for paraquat is not by ion exchange but by adsorption.

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