Enhancing Effect of Sodium Chloride on *in vitro* Adsorption of Paraquat onto Activated Carbon

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Introduction

The usefulness of activated carbon for the primary treatment of various poisonings caused by swallowing of drugs or poisons has been recognized^{1, 2)}. In acute poisoning, activated carbon has been administered for the inhibition of absorption of drugs or poisons in the digestive tract, and its efficacy has been reported^{3, 4)}.

Paraquat has been widely used as a superior herbicide and is unlikely to produce serious problems when properly used^{5, 6)}. 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 chemicals⁷⁾. The LD₅₀ (oral) of paraquat for man is assumed to be 40 mg/kg⁸⁾. In order to prevent accidental poisoning, emetics in 1979, blue azo dye in 1982 and specific odor substances in 1985 were added to paraquat preparations⁷⁾. Furthermore, the production of paraquat preparations of high concentration (24%) was discontinued in July 1986 in Japan.

At present, no specific and effective antidote for paraquat poisoning is available. It was reported that the adsorption of paraquat *in vitro* onto activated carbon for the primary treatment of paraquat poisoning was more effective in normal saline solution^{9, 10)}. However, little work on the influence of the sodium chloride concentration on the adsorption capacity of activated carbon has been done so far. In this study, the influence of the sodium chloride concentration on the *in vitro* adsorption of paraquat onto activated carbon was investigated.

Materials and Methods

The paraquat used as an adsorbate was a commercial preparation (Gramoxone S, Nihon Nohyaku Co., Ltd.) and its concentration was indicated as 24%. Activated carbon used as the adsorbent was Shirasagi G2C (Takeda Chemical Ind., Ltd.). The sodium chloride was of extra pure reagent grade (Nakarai Tesque Inc.).

Adsorption isotherms were obtained as follows. A weighed amount of activated carbon, 0.2~0.5g, was shaken with 50ml of paraquat solution of *ca.* 200~3500mg/L for 24 hrs at 37°C. After filtration, the paraquat concentration in the filtrate was measured by a colorimetric method using an alkaline sodium dithionite solution¹¹⁾. It took 24 hrs or less to attain equilibrium adsorption.

The adsorption rate was measured in the paraquat-solution adsorbent system at 37°C. Five grams of activated carbon was added to one liter of a stirred paraquat solution (*ca.* 800mg/L). Five milliliters of the suspension was sampled at regular intervals, and the paraquat concentrations were measured.

Ratios of sodium chloride addition to paraquat solution were 0.1, 0.3, 0.5, 0.7 and 0.9%.

Results

Addition of sodium chloride showed no effect on the absorbance at 600 nm as measured by colorimetric determination of the paraquat concentration.

Adsorption isotherms of paraquat at 37°C are shown in Figure 1. The amount of paraquat adsorbed increased with the increase in the amount of sodium chloride added. Table 1 indicates the amount of paraquat adsorbed at each equilibrium concentration. The amount adsorbed was calculated using the Freundlich equation as expressed by the following formula,

$$\text{Log } V = 1/n \text{ Log } C + \text{Log } k$$

where V is the equilibrium amount adsorbed and C is the equilibrium concentration. Both $1/n$ and k are constants. Amounts adsorbed were increased by the addition of sodium chloride. At an equilibrium concentration of 1mg/L, the amount of paraquat adsorbed in 0.1% addition was about five times greater than that in sodium chloride-free solution. For other equilibrium concentrations, the amount of paraquat adsorbed also increased with the addition of sodium chloride.

The relationships between the amount of paraquat adsorbed at each equilibrium concentration and the concentration of sodium chloride in solution are shown in Figure 2. The amount adsorbed was approximately proportional to the concentration of sodium chloride in solution. It was recognized that the addition of sodium chloride increased the amount of paraquat adsorbed onto the activated carbon.

Fig. 1 Adsorption Isotherm of Paraquat at 37°C

NaCl (%) : ●:0, ○:0.1, ▲:0.3, △:0.5, ■:0.7, □:0.9

Table 1 Equilibrium Amount of Paraquat Adsorbed

NaCl (%)	Amount Adsorbed (mg/g)			
	v at 1 mg/L	v at 10 mg/L	v at 100 mg/L	v at 1000 mg/L
0	1.55	4.63	13.86	41.45
0.1	7.73	15.31	30.29	59.95
0.3	8.95	17.82	35.51	70.75
0.5	9.08	18.37	37.17	75.23
0.7	11.21	21.66	41.86	80.90
0.9	9.42	19.42	41.37	86.71

The amount of activated carbon needed for 90% removal of paraquat is indicated in Table 2. The amount of activated carbon was calculated according to the method of Ogino *et al*⁽¹¹⁾. The equation can be expressed in the following form:

$$M = [C_1 - C_2] / V$$

where M is the amount of activated carbon needed for 90% removal, C_1 is the initial concentration, C_2 is the one-tenth concentration of C_1 , and V is the amount adsorbed at C_2 . The amount needed for 90% removal in the initial paraquat concentration of 1000mg/L was the largest in the sodium chloride-free solution and smallest in the solution with 0.7% addition of sodium chloride. The difference in the amount of activated carbon needed for 90% removal between the sodium chloride-free case and the case with 0.7 or 0.9% addition of sodium chloride was three times or more with an initial paraquat concentration of 1000mg/L. The difference with an initial concentration of 10mg/L was about 5-7 times.

In the evaluation of adsorbent, the adsorption rate is another factor to be determined. In Figure 3, the time course of the paraquat adsorption is shown. The addition of sodium chloride accelerated the adsorption rate of paraquat onto activated carbon.

Fig. 2 Relationships between the Amount of Paraquat Adsorbed and the Concentration of Sodium Chloride

Table 2 Amount of Activated Carbon needed for 90 % Removal of Paraquat at Various Initial Concentrations

NaCl (%)	Amount of Activated Carbon (g)		
	1000 mg/L	100 mg/L	10 mg/L
0	64.9	19.4	5.8
0.1	29.7	5.9	1.2
0.3	25.3	5.1	1.0
0.5	24.2	4.9	1.0
0.7	21.5	4.2	0.8
0.9	21.8	4.6	1.0

Fig. 3 Time Courses of Paraquat Adsorption in Various Concentration of NaCl
NaCl (%) : ●:0, ○:0.1, ▲:0.3, △:0.5, ■:0.7, □:0.9.

Discussion

Activated carbon has been used for the primary treatment of drug poisoning^{3, 4}). The efficacies of activated carbon, natural aluminum silicate, bentonite, and a cation exchange resin for paraquat poisoning have been reported^{13~16}). In recent years, the high removal capacities of kayexalate and kalimate, which are medical resins for the treatment of hyperkalemia, for paraquat have been reported^{17, 18}). Although the removal capacity of activated carbon for paraquat is inferior to that of medical resin, activated carbon has been evaluated as a safe and effective gastrointestinal adsorbent. For paraquat removal by activated carbon, the following methods are proposed as a means of improving the adsorption capacity; the screening of a suitable activated carbon or surface modification of activated carbon by plasma irradiation, wet oxidation, and the choice of a suitable solvent in preparation of the carbon suspension. We have previously reported that the amount of paraquat adsorbed was large in normal saline solution^{9, 10}). In this paper, we discussed the change in the amount of paraquat adsorbed by activated carbon in solutions with different sodium chloride concentrations.

The enhancing effect of saline purgatives on the *in vitro* adsorption of drugs by activated carbon has been reported. Ryan *et al*¹⁹) reported the effect of magnesium citrate on the ability of activated carbon to adsorb sodium salicylate. They found that more salicylate was adsorbed onto activated carbon in the presence of magnesium citrate than in water alone. They did not report the mechanism of the enhanced adsorption of salicylate onto activated carbon in the presence of magnesium citrate, but the effects of pH and ionic strength have been excluded. Lapierre *et al*²⁰) also reported that magnesium citrate actually enhanced the ability of activated carbon to adsorb aspirin in a simulated intestinal solution. They thought the mechanism of enhanced adsorption of aspirin was due to a pH change in the simulated intestinal solution brought about by the addition of magnesium citrate, thus resulting in less ionized salicylate and enhanced binding.

In our experiments, the adsorption capacity of activated carbon was observed to be enhanced by the addition of sodium chloride. We assumed that the reason for the increased adsorption capacity for paraquat by activated carbon in the presence of sodium chloride was as follows. The dissociation of paraquat in solution was inhibited by the addition of sodium chloride, that is, the phenomenon of salting out occurred in solution. Therefore, paraquat was adsorbed more abundantly onto the activated carbon.

It was concluded that the addition of sodium chloride to a carbon suspension was effective to promote adsorption removal of paraquat.

Summary

The enhancing effect of sodium chloride addition on the adsorption of paraquat onto activated carbon was discussed from the standpoints of equilibrium amount adsorbed and adsorption rate *in vitro*.

The amount of paraquat adsorbed was increased by the addition of sodium chloride. The amount adsorbed with 0.1% addition was about five times greater than that in sodium chloride-free solution at an equilibrium concentration of 1 mg/L. The adsorption rate of paraquat onto activated carbon was also accelerated by sodium chloride addition. Kinetic constants in 0.1% and 0.9% sodium chloride solution were about 1.4 and 2.0 times greater, respectively, than that in sodium chloride-free solution.

It was confirmed that paraquat removal by activated carbon was enhanced by sodium chloride addition. The reason was assumed to be the interrupted dissociation of paraquat in solution caused by sodium chloride addition.

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活性炭へのパラコート吸着における塩化ナトリウムの促進効果

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活性炭によるパラコート除去における塩化ナトリウムの促進効果について、吸着量および吸着速度の観点より考察した。

パラコート吸着量は、塩化ナトリウムの添加により増大した。平衡濃度 1 mg/L における吸着量を比べると、0.1% の塩化ナトリウム添加で、無添加の場合より、約 5 倍高値を示した。

活性炭に対するパラコートの吸着速度においても、塩化ナトリウムの添加により促進効果を認めた。0.1% および 0.9% の塩化ナトリウム添加における速度定数は、無添加の場合より約 1.4 倍および 2 倍高値を示した。

活性炭によるパラコート除去において、塩化ナトリウム添加による促進効果が認められた。塩化ナトリウム添加により、溶液中のパラコートの解離が妨げられることによるものであると推察した。

Key words: Paraquat removal, Activated carbon, Addition of sodium chloride, Enhancing effect
パラコート除去, 活性炭, 塩化ナトリウム添加, 促進効果

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