

原 著

塩化ナトリウム添加による活性炭へのパラコート およびジクワット吸着の促進

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In vitro acceleration of paraquat and diquat adsorption onto activated carbon by addition of sodium chloride

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要約

急性農薬中毒における経口吸着剤としての活性炭の効果的な使用を指向し、塩類共存下における活性炭のパラコートおよびジクワット吸着特性について検討した。活性炭へはパラコートの方がジクワットよりも優先的に吸着されることを認めた。このことは両農薬成分の一電子還元電位の違いに基づくものと推察される。また塩化ナトリウムの共存により、活性炭へのパラコートおよびジクワット吸着促進が認められた。塩化ナトリウム添加による活性炭へのパラコートおよびジクワットの吸着量および吸着速度の増大は、塩素陰イオンの吸着に基づく活性炭素面の電気二重層形成による静電的引力の増大に起因するものと推察される。
(臨床環境 7 : 74~79, 1998)

Abstract

Adsorption characteristics of paraquat and diquat onto activated carbon from saline solution was investigated for the effective use as an oral adsorbent. The amount of paraquat adsorbed onto activated carbon was larger than that of diquat adsorbed. It is assumed that the difference of the adsorption characteristics are due to the difference of one-electron reduced potential of constituents. Then the acceleration of adsorption removal of paraquat and diquat onto activated carbon by the addition of sodium chloride was recognized. The acceleration of paraquat and diquat adsorption might be the result of the increase of electrostatic interaction between the surface on which an electrical double layer has formed by the adsorption of chloride anion and paraquat and/or diquat.
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《Key words》 paraquat, diquat, activated carbon, saline addition, adsorption characteristics

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I. Introduction

Paraquat has been widely used as herbicide because of its superior herbicidal effect. And it is reported that paraquat is unlikely to give rise to serious problems when properly used^{1,2)}. Since the report of two cases of death by ingestion of paraquat in 1966³⁾, cases of paraquat poisoning increased and became a social problem in Japan⁴⁾. In order to reduce the poisoning, emetics, blue azo dye and specific odor substances were added to paraquat preparations in 1979, 1982 and 1985⁴⁾, and the production of highly concentrated paraquat preparation (24%) has been discontinued since 1986. Now the mixed preparation (paraquat 5% and diquat 7%) is on the market. Although paraquat concentration in the mixed preparation has lowered, the mortality by misapplication and ingestion is still high⁵⁾. The effective therapy for the poisoning induced by misapplication and ingestion of mixed preparation of paraquat has not been established yet.

Activated carbon is a safe and effective adsorbent for the emergency treatment of drug poisoning, and commonly used for removing toxic substances from the digestive tract^{6,7)}.

In the primary therapy of acute poisoning, gastrointestinal lavage, administration of adsorbent, forced diuresis, hemoperfusion and so on are performed. Warm water or physiological saline solution are usually used for gastrointestinal lavage. The finding of a suitable combination of adsorbent and solution for lavage to effectively remove of toxic substances from digestive tract is important.

In this investigation, we examined *in vitro* whether paraquat and diquat can be removed by activated carbon from a solution containing paraquat, diquat and sodium chloride.

II. Materials and Methods

We used the mixed preparation (paraquat 5%,

diquat 7%) which was a commercial preparation (Pregrox-L, Nihon Noyaku Co. Ltd.). Measurement of paraquat and diquat were performed using standard solution containing pure paraquat and diquat (Wako Pure Chem. Co. Ltd). We used two kinds of activated carbons of commercial products having particle sizes of 20-32 mesh. Before use, the activated carbon was washed in distilled water until no fine carbon particle was visible. The activated carbon was dried at 110°C for 48 hours, and kept in a desiccator. The physicochemical properties of activated carbon are shown in Table 1.

Table 1 Properties of Activated Carbon.

Adsorbent	Surface Area (m ² /g)	Pore Volume (ml/g)		Surface pH
		r<20Å	r<100Å	
AC-1	1081.1	0.472	0.520	6.5
AC-2	850.1	0.458	0.501	5.9

The time-courses change in the amount of paraquat and diquat adsorbed onto activated carbon was as follows. Five grams of activated carbon were placed in one liter of paraquat and diquat mixture solution (which had been diluted 100 times), and then stirred (300rpm) at 37°C. Five milliliters of the supernatant solution were taken at regular intervals and the concentration of paraquat and diquat was measured.

Paraquat was measured at 600nm by a calorimetric method using an alkaline sodium dithionite solution⁸⁾. Diquat concentration was measured at 310nm with a spectrophotometer (Hitachi model 101)⁹⁾.

The concentration of sodium chloride in the paraquat and diquat mixture solution was 0.1, 0.5 and 0.9%.

III. Results

The time-course change in the amount of paraquat adsorbed onto the activated carbon is

shown in Figure 1. The amount of paraquat adsorbed increased with the increase in time. The increase in the concentration of sodium chloride increase the amount of paraquat adsorbed onto the activated carbon. The amount of paraquat adsorbed 120 minutes after the start of

experiment in the 0.9% sodium chloride solution was 2.7 fold (AC-1) and 1.9 fold (AC-2) as much as the amount of paraquat adsorbed in the sodium chloride free solution.

The time-course change in the amount of diquat adsorbed is shown in Figure 2. The

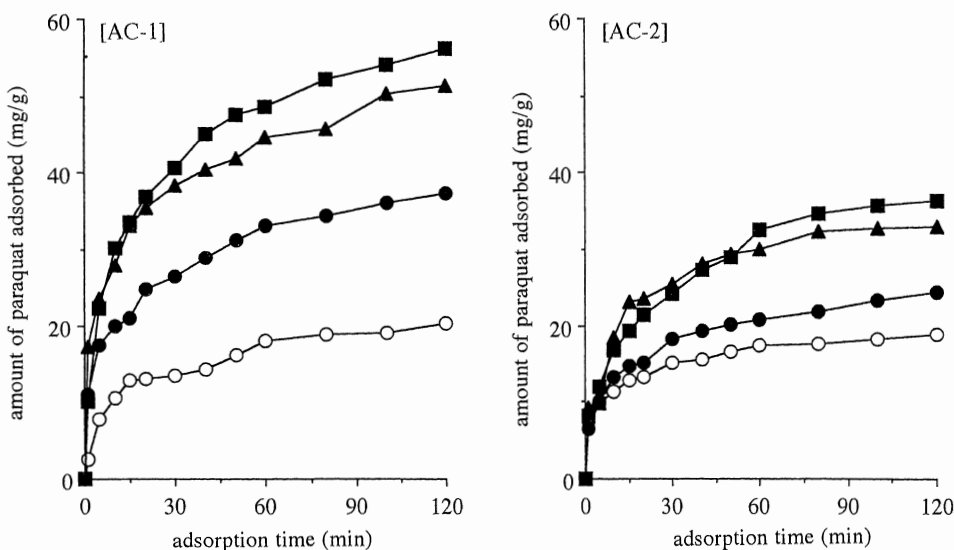


Fig.1 Time Course of Paraquat Adsorption onto Activated Carbon from Saline Solution. concentration of sodium chloride (%): ○; 0, ●; 0.1, ▲; 0.5, ■;0.9. weight of adsorbent: 5.0g, solution: 1L of solution diluted 100 times of commercial product, stirring conditions: 300 rpm at 37°C.

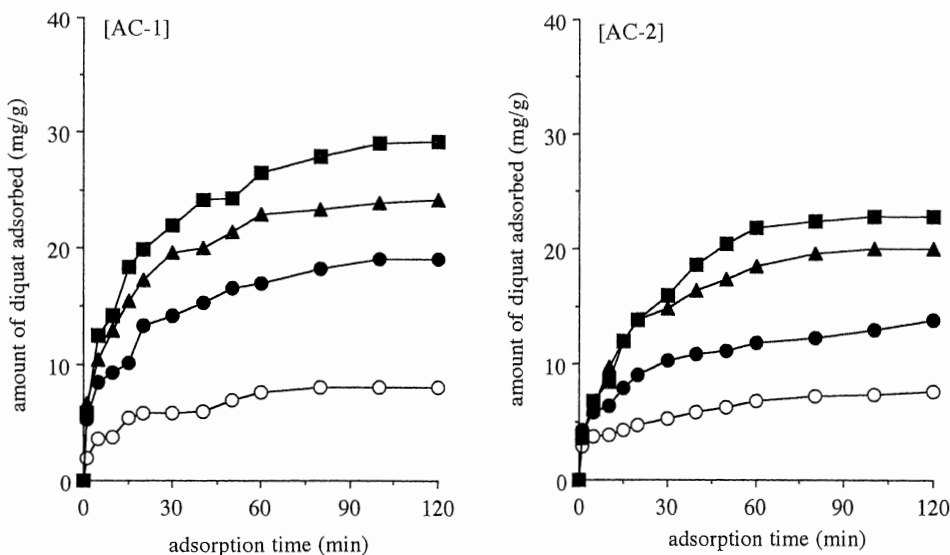


Fig.2 Time Course of Diquat Adsorption onto Activated Carbon from Saline Solution. concentration of sodium chloride (%): ○; 0, ●; 0.1, ▲; 0.5, ■;0.9. weight of adsorbent: 5.0g, solution: 1L of solution diluted 100 times of commercial product, stirring conditions: 300 rpm at 37°C.

amount of diquat adsorbed onto the activated carbon increased with the increase in the concentration of sodium chloride in a similar manner as that of paraquat. The amount of diquat adsorbed after 120 minutes in the 0.9% sodium chloride solution was 3.6 fold (AC-1) and 3.0 fold (AC-2) as much as that in the sodium chloride free solution.

These results also indicate that the amount of paraquat adsorbed onto the activated carbon was larger than that of diquat, and that the adsorbed amount of paraquat and diquat increased with the increase in the concentration of sodium chloride.

To elucidate the rate of adsorption of paraquat and/or diquat onto the activated carbon, the kinetic constant was calculated by applying the formula of zero order reaction to the curves of change in the adsorbed amounts of paraquat and diquat. The results are indicated in Table 2. For both paraquat and diquat, the higher the concentration of sodium chloride, the larger the kinetic constant. Therefore the adsorption rate of paraquat and diquat onto the activated carbon increased with the increase in the concentration of sodium chloride.

Table 2 Kinetic Constant of Paraquat and Diquat Adsorption by Activated Carbon.

NaCl (%)	Kinetic Constant ($\text{mg/g}\cdot\text{min}^{-1}$)	
	Paraquat	Diquat
[AC-1]		
0	0.136	0.053
0.1	0.234	0.125
0.5	0.306	0.154
0.9	0.369	0.194
[AC-2]		
0	0.106	0.048
0.1	0.151	0.086
0.5	0.216	0.141
0.9	0.256	0.173

IV. Discussion

The usefulness of activated carbon for a primary treatment for various types of poisoning caused by swallowing of drugs or poisons has been recognized^{6,7)}. In acute poisoning, the activated carbon has been used for inhibition of absorption of drugs or poisons in the digestive tract with success¹⁰⁾.

We found that the adsorbed amount of paraquat was larger than that of diquat. Because paraquat has stronger toxicity than diquat, the foregoing evidence has an advantage to the treatment of paraquat poisoning. In general, the activated carbon adsorbs non-polar substances. The one-electron reduced potential of paraquat and diquat is -0.43V and -0.36V , respectively¹¹⁾. Therefore the polarity of paraquat is considered stronger than that of diquat. It is concluded that the difference in adsorbed amount between paraquat and diquat onto the activated carbon is due to the strength of polarity of paraquat and diquat.

The effect of magnesium citrate on the ability of activated carbon to adsorb sodium salicylate or aspirin *in vitro* was reported^{12,13)}. Honda *et al*¹⁴⁾ reported the enhanced adsorption of paraquat in the presence of sodium chloride and magnesium sulfate onto the activated carbon. Lapiere *et al*¹³⁾ thought that the mechanism of the enhancement of aspirin adsorption onto the activated carbon was due to the change in pH in the solution brought about by addition of magnesium citrate, which resulted in less production of ionized salicylate. Honda *et al*¹⁴⁾ also thought that the dissociation of paraquat in solution was inhibited by the addition of saline, that is, salting-out took place in the solution. This is the reason why there is enhancement of paraquat adsorption onto the activated carbon. However, as the crystal structure of paraquat and diquat is ionic and these substances dissociates perfectly in the solution. Therefore, the salting-out may not take

place in the solution.

Regarding saline adsorption onto the activated carbon, anion is specifically adsorbed. Afterward, an electrical double layer is formed on the surface of activated carbon, which attracts cation in solution¹⁵⁾. It is proposed that paired anions of paraquat cation and diquat cation are attracted by the surface of activated carbon and then paraquat and diquat cations are adsorbed. The surface oxygen groups inhibit approach of anions onto the surface of activated carbon because of the electrical repulsive force between surface oxygen groups and anions. The enhancing effect of sodium chloride on the removal of paraquat and diquat induced by the activated carbon *in vitro* might be the result of the increase of electrostatic interaction between the surface on which an electrical double layer has formed by salts and paraquat and/or diquat.

V. Conclusion

For the purpose of the effective use of activated carbon in the acute poisoning, adsorption characteristics of paraquat and diquat onto activated carbon from sodium chloride solutions with different concentration were examined. The increase in the concentration of sodium chloride increase the amounts of paraquat and diquat adsorbed onto the activated carbon. The kinetic constant for paraquat and diquat removal was larger with the increase in the concentration of sodium chloride. It was concluded that sodium chloride accelerated the adsorption of paraquat and diquat onto the activated carbon in the solution.

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