

原 著

繊維状活性炭によるジクワット吸着

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Adsorption of Diquat by Activated Carbon Fiber

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要約

ジクワットの誤飲、誤用等による急性農薬中毒事故の初期処置における経口吸着剤としての繊維状活性炭の評価について基礎的検討を試みた。吸着剤に対するジクワットの吸着等温線より算出した吸着量については、生理食塩水中からの吸着量が精製水中からの吸着量よりも上回った。また吸着剤に対するジクワットの吸着速度についても、生理食塩水中からの方が精製水中からよりも速く除去し、塩化ナトリウム添加による吸着促進効果が認められた。またジクワットに対する吸着特性と吸着剤の諸物性の関係については、比表面積、細孔容積が高値であるほど、良好なジクワット吸着特性を示すことが推察された。

(臨床環境 5 : 18~22, 1996)

Abstract

For evaluation of the efficacy of activated carbon fiber (ACF) as an adsorbent in acute diquat intoxication, the adsorption characteristics of diquat in purified water and in physiological saline solution were investigated. The amount of diquat adsorbed onto ACF from physiological saline solution containing diquat was larger than that from purified water containing diquat. The enhancing effect of sodium chloride on removal of diquat by ACF was recognized. The adsorption rate of diquat onto ACF was also enhanced in the presence of sodium chloride. It is assumed that the adsorbent which has large surface area and pore volume adsorbs diquat abundantly.

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《Key words》 diquat intoxication, activated carbon fiber, adsorption characteristics, physiological saline solution

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Diquat(1,1'-ethylene-2,2'-dipyridylium dibromide) is a strong herbicide, similar to paraquat. In general, agricultural chemicals are unlikely to give rise to serious health problems when properly used¹⁾. However, there are number of cases of acute intoxication due to accidental, suicidal, or homicidal ingestion of agricultural chemicals²⁾.

The LD₅₀ of orally administered diquat has been reported as 400~440mg/kg in rats. This value is about three times higher than that of paraquat (130 mg/kg)³⁾. Although the LD₅₀ is smaller than that of paraquat, the toxicity of diquat is almost equal to that of paraquat when the same amount of diquat or paraquat is ingested. At present, two kinds of diquat preparations are on the market in Japan; diquat (30%) preparation and diquat (7%) + paraquat (5%) preparation. Production of preparation containing high concentration of paraquat (24%) discontinued in July 1986.

While many cases of paraquat intoxication have been reported, there are only a few reports on diquat intoxication. Seo *et al.*⁴⁾ has reported cases of acute diquat intoxication, in which 4 out of 6 died.

The principle of emergency treatment for diquat intoxication is almost the same as that for paraquat intoxication. The basic treatment is the selective excretion of toxic substances out of the body by means of gastrointestinal lavage as well as the oral administration of adsorbent. Among adsorbents, activated carbon has been evaluated as a reliable, safe and inexpensive adsorbent and is recommended for use when removal of toxic substances is required^{5,6)}. In recent years, activated carbon fiber (ACF), a new type of high-functional activated carbon which is rich in micro pore volume, has been developed, and a beneficial effect of ACF on acute intoxication is expected. However, little is known about removal of toxic substances by ACF in acute intoxication.

When we use an adsorbent to remove a toxic substance, we suspend it in water or physiological saline solution to make a solution containing the adsorbent for gastrointestinal lavage.

In the present investigation, we studied the adsorption removal of diquat by ACF from solutions containing diquat *in vitro* to find effective treatment of acute diquat intoxication using ACF.

MATERIALS AND METHODS

Diquat used for adsorption experiments was a commercial preparation (Reglox, Nihon Noyaku Co. Ltd., Tokyo). Diquat used for construction of a calibration curve was purchased from Wako Pure Chem. Ind. Ltd., Osaka, and its grade was for detecting residual agricultural chemicals.

ACFs were obtained from Osaka Gas Co. Ltd., Osaka. The physical properties of ACFs (A-10 and A-20) are shown in Table 1.

Table 1 Properties of ACFs

Adsorbent	Surface area (m ² /g)	Pore volume (mL/g)	Surface pH
A-10	918.1	0.510	7.11
A-20	1754.0	0.924	6.35

Accurately weighed ACF (about 20~50mg) was shaken with 50 mL of a solution containing known concentrations of diquat (100~1000mg/L) in purified water or in physiological saline solution at 37°C. After 24 hours, the concentration of unadsorbed diquat in the solution was determined spectrophotometrically at 310 nm with a spectrophotometer (Hitachi model 100-10)⁷⁾. The amount of diquat adsorbed was calculated from the difference between the initial total amount of diquat and the amount of unadsorbed diquat.

The time-course of adsorption was also studied at 37°C in purified water and in physiological saline solution. Five grams of ACF were added to 1000 mL of a stirred diquat solution (300rpm, ca. 2000 mg/L) and the diquat concentrations in the solution were measured at regular intervals.

The surface area and the pore size distribution of ACFs were measured with a B.E.T. apparatus (Shibata P-700) using nitrogen gas at its boiling temperature (-196°C). The pore volume was calculated by the method

of Dollimore and Heal⁸⁾. Surface pH of ACF was measured by the method of Urano *et al.*⁹⁾.

RESULTS AND DISCUSSION

Adsorption isotherms of diquat onto ACF at 37°C are shown in Figure 1. The adsorption isotherms of diquat

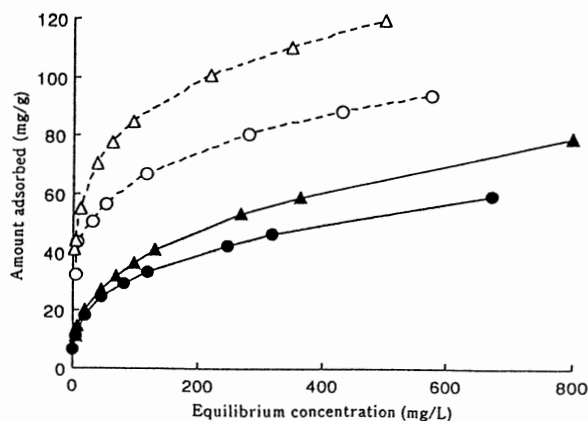


Fig. 1 Adsorption isotherm of diquat onto ACF at 37°C. full line: in purified water, dotted line: in physiological saline solution.

●,○: A-10, ▲,△: A-20.

onto ACF from both purified water containing diquat and physiological saline solution containing diquat were the Freundlich type. Figure 1 shows that the amount of diquat adsorbed from physiological saline solution containing diquat was larger than that from purified water containing diquat.

The amount of diquat adsorbed was calculated by the Freundlich equation, and is shown in Table 2. The

Table 2 Equilibrium amount of diquat adsorbed onto ACFs

adsorbent	amount adsorbed (mg/g)		
	at 1 mg/L	at 10 mg/L	at 100 mg/L
A-10	6.6 ^a	14.3 ^a	31.2 ^a
	24.2 ^b	39.6 ^b	64.7 ^b
A-20	6.6 ^a	15.6 ^a	36.8 ^a
	33.5 ^b	53.6 ^b	85.8 ^b

^a; from purified water, ^b; from physiological saline solution.

amount adsorbed from the physiological saline solution containing diquat was larger than that from the purified water containing diquat at each equilibrium concentration. The ratio of the amount of diquat adsorbed from the physiological saline solution to that from the purified water was 3.7~5.1 at 1 mg/L, 2.8~3.4 at 10 mg/L and 2.1~2.3 at 100 mg/L of equilibrium concentration of diquat.

Figure 2 shows the time-course change of the amount

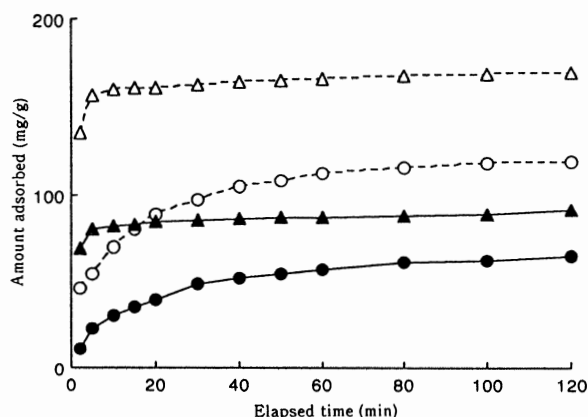


Fig. 2 Time-course change of the amount of diquat adsorbed onto ACF at 37°C.

full line: in purified water, dotted line: in physiological saline solution,

●,○: A-10, ▲,△: A-20

of diquat adsorbed at 37°C in the purified water containing diquat and in the physiological saline solution containing diquat. The amount of diquat adsorbed from the physiological saline solution was larger than that from the purified water. This order was similar to that for the equilibrium adsorption. The amount of diquat adsorbed onto A-10 gradually increased with the increase in time, whereas that of diquat adsorbed onto A-20 rapidly increased within a few minutes.

Adsorption site for adsorbate exists near the surface of ACF¹⁰⁾. Therefore, the adsorption rate would not be depressed by intraparticle diffusion. The degree of activation, that is the amount of diquat adsorbed, was higher when A-20 was used, and it is thought that competition for the adsorption site between A-20 and

diquat is little. Therefore, it is concluded that the amount of diquat adsorbed onto A-20 was rapidly increased within a few minutes.

Although the surface area and the pore volume of A-20 were large, the adsorption capacity of diquat onto A-20 per unit surface area and per unit pore volume was smaller than that onto A-10. Therefore, the physical properties such as surface area and pore volume cannot be evaluated as the first dominant factor in removal of diquat by ACF.

The effect of sodium chloride to enhance adsorption of diquat onto ACF was recognized. The effect of salts on the adsorbability of activated carbon has been reported. It is reported that the adsorption of paraquat onto activated carbon is enhanced in the presence of sodium chloride^{11,12)}. The structure and properties of diquat are almost the same as those of paraquat. The fact that the amount of diquat adsorbed by ACF increased in the presence of sodium chloride is in accord with the experiments with paraquat¹³⁾. Magnesium citrate also increases adsorbability of activated carbon; Ryan *et al.*¹⁴⁾ reported that more salicylate was adsorbed onto activated carbon in the presence of magnesium citrate. Lapiere *et al.*¹⁵⁾ also reported the effect of magnesium citrate to enhance the adsorption of aspirin to the activated carbon. They think that the enhanced adsorption is due to the salting-out effect. That is, it is assumed that the enhanced adsorption is due to the interruption of dissociation of adsorbate in solution caused by the addition of salts. However, it can not be ignored that the change in the surface electric charge of adsorbent by saline addition. Urano *et al.*⁹⁾ reported on the adsorption of salts onto activated carbon and the formation of electric double layer due to the adsorption of anion. Therefore, it is assumed that the interaction between diquat cation and the electric charge of adsorbent is strengthened by the addition of sodium chloride.

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