

原 著

キトサン誘導体によるパラコートおよびジクワットの除去

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Paraquat and diquat removal by chitosan derivatives

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要約

急性パラコートおよびジクワット中毒における経口吸着剤としてのキトサン誘導体の評価に関する基礎的検討を試みた。キトサン誘導体に対してはパラコートよりもジクワットの方が良好な吸着特性を示し、この結果はパラコートとジクワットの極性強度の差に起因することが示唆された。またキトサン誘導体のうち、カルボキシル基を有するもの(C-10)は、スルホニル基を有するもの(SU-10)よりも吸着特性に優れていた。この違いは両誘導体のイオン交換能の差によるものと推測された。生理食塩水中からの中毒物質の吸着除去特性は、精製水中での結果よりも劣っており、共存塩である塩化ナトリウムの妨害効果が認められた。共存塩のない溶液中からパラコートおよびジクワットを除去する場合には、陽イオン交換能の大きいキトサン誘導体を用いることが至適な条件であることが結論づけられた。

(臨床環境12:27~31, 2003)

Abstract

The evaluation of chitosan derivatives as oral adsorbent for acute paraquat and diquat poisoning was investigated *in vitro*. The adsorption characteristics for diquat onto chitosan derivatives were better than those for paraquat. It was assumed that the difference was depend on the strength of polarity of paraquat and diquat. The adsorption characteristics onto carboxyl chitosan (C-10) were better than those of sulfonyl chitosan (SU-10). It could be explained by the difference of cation exchange capacity of chitosan derivatioives. And it was recognized that the adsorption characteristics from

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physiological saline solution were poor due to the inhibition of sodium chloride.

It was concluded that the use of chitosan derivatives which having large cation exchange capacity and from sodium chloride free solution was suitable for paraquat and diquat removal.

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«Key words» paraquat, diquat, oral adsorbent, chitosan derivatives, acute poisoning

I. Introduction

Chemicals are indispensable for modern agriculture and used for the purpose of controlling vermin and weeds. Alkylbipyridylum herbicides such as paraquat and diquat have been used all over the world due to their superior herbicidal effect. It is reported that a herbicide is unlikely to produce serious problems when properly used^{1,2)}. However many people have died through accidental, suicidal or homicidal ingestion of preparations contained paraquat and/or diquat^{3~5)}.

No specific and effective antidote for paraquat and/or diquat poisoning is available up to the present. Gastrointestinal lavage, administration of adsorbents and/or purgatives, forced diuresis, hemoperfusion and so on are performed for removing toxic substances⁶⁾. In primary therapy for acute paraquat and/or diquat poisoning, adsorbents such as activated carbon, clay minerals and medical cation exchange resins are administered orally^{7~10)}.

Chitin, β -(1-4)-poly-N-acetyl-D-glucosamine is a natural polymer that is bio-produced in nature, and the bio-production amount is the next large amount to cellulose. Chitosan is a polymer obtained by deacetylation of chitin. In recent years, the research and development on the effective utilization of chitinous substances have advanced in the fields of environmental and pharmaceutical sciences^{11~14)}. However, little studies on the evaluation of chitinous substances as an oral adsorbent have been done so far¹⁵⁾. In this investigation, we discuss the paraquat and diquat removal by chitosan

derivatives *in vitro*.

II. Materials and Methods

The mixed preparations of paraquat and diquat (Pregrox L) in the adsorption experiments were obtained from Nihon Noyaku Co. Ltd. The standard solutions for calibration curves were prepared by using paraquat and diquat for the test of agricultural chemical residue (Wako Pure Chem. Co. Ltd.).

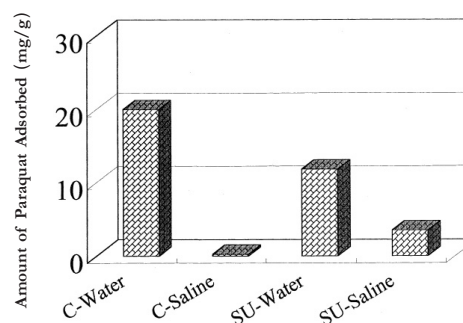


Fig. 1 Comparison of amount of paraquat adsorbed at 100 mg/L.

As adsorbent, carboxyl chitosan (C-10) and sulfonyl chitosan (SU-10) made by Fuji Spinning Co. Ltd. were used. Their particle sizes are 0.9-1.0 mm and cation exchange capacity were $200\mu\text{eq/mL}$ (C-10) and $70\mu\text{eq/mL}$ (SU-10) from technical data of manufacture, respectively.

The adsorption isotherms of paraquat and diquat onto modified chitosan were measured as follows: 500mg of adsorbent was shaken with 40mL of the solution of mixed preparations with different concentration by dilution for 24 hours at 310K. After filtration, un-

adsorbed paraquat and diquat concentrations in the filtrate were measured at 255 and 310nm with a spectrophotometer (Shimadzu, UV-1200), respectively. The amounts of paraquat and diquat adsorbed were calculated from the difference between the initial total amount and the amount of the unadsorbed. The time course of adsorption was also examined. Five grams of adsorbent were placed in 200mL of the solution of mixed preparations (which had been diluted 100 times), and then stirred (300rpm) at 310K. Two milliliters of the supernatant solution were taken at regular intervals and the concentrations of paraquat and diquat were measured. Diluents used were water and physiological saline solution.

III. Results

The equilibrium amounts adsorbed at 100 mg/L of equilibrium concentration were read off from adsorption isotherms, and then the amount of paraquat and diquat adsorbed were shown in Figures 1 and 2, respectively. Both paraquat and diquat, the amount adsorbed from physiological saline solution was less than that from water. The amounts of paraquat adsorbed onto C-10 and SU-10 from water were 80 times and 3.4 times greater than those from physiological saline solution, respectively (Figure 1). And the amounts of diquat adsorbed onto C-10 and SU-10 from water were 85 times and 3.2 times greater than those from physiological saline solution, respectively (Figure 2). The amount adsorbed from water onto C-10 was greater than that onto SU-10. However, the amount adsorbed from physiological saline solution onto C-10 was smaller than that onto SU-10.

In the evaluation of adsorbent, the adsorption kinetic is another factor to be determined. The time courses of paraquat adsorption from

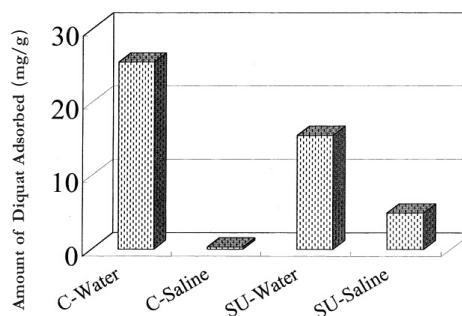


Fig. 2 Comparison of amount of diquat adsorbed at 100 mg/L.

water and physiological saline solution are shown in Figure 3. The amount of paraquat adsorbed was abruptly increased within 5 minutes of elapsed time, and then reached at plateau within 30 minutes of elapsed time. Paraquat removal from water was more rapid than that from physiological saline solution. The time courses of diquat adsorption are shown in Figure 4. The amount of diquat adsorbed was abruptly increased within 5 minutes of elapsed time, and then reached at plateau within 30 minutes of elapsed time. Diquat removal from water was more rapid than that from physiological saline solution in analogy with paraquat.

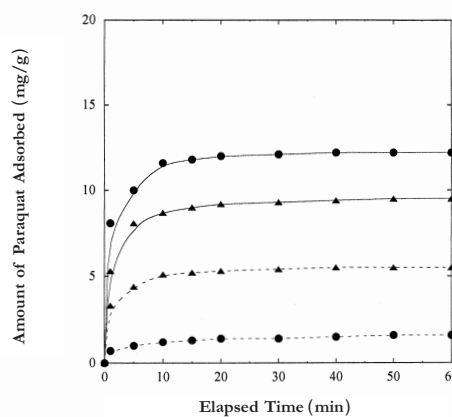


Fig. 3 Time courses of paraquat adsorption onto chitosan derivatives at 310K.

• : C-10, ▲ : SU-10,
 full line: from water,
 dotted line: from physiological saline solution.

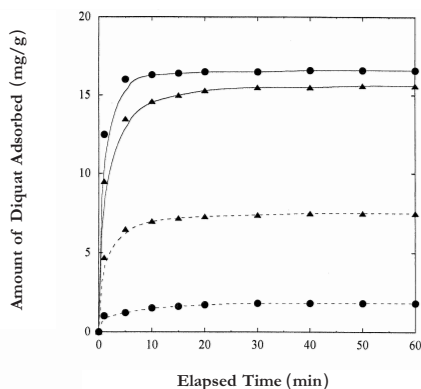


Fig. 4 Time courses of diquat adsorption onto chitosan derivatives at 310K.

•: C-10, ▲: SU-10,
full line: from water,
dotted line: from physiological saline solution.

IV. Discussion

Chitinous substances are natural polysaccharides, and are the second abundant most biopolymer in nature after cellulose. They are nontoxic, biodegradable and biocompatible. However, little studies on the effective use of chitinous substances as oral adsorbent have been done so far¹⁵⁾. Therefore, the removal of paraquat and diquat for the primary treatment in acute poisoning by chitosan derivatives *in vitro* are discussed.

The amount adsorbed and adsorption rate of diquat were better than those of paraquat. Chitosan derivatives used have hydrophilic functional groups and their surface is more hydrophilic. Therefore, it is predicted that they adsorb polar substances. The one electron reduced potential of paraquat and diquat is $-0.43V$ and $-0.36V$, respectively. That is, diquat is liable to receive an electron than paraquat¹⁶⁾. In other words, the polarity of diquat is stronger than that of paraquat. Therefore, it is assumed that the difference in the adsorption characteristics between paraquat and diquat is due to the difference in strength of polarity of paraquat and diquat.

The cation exchange capacity of C-10 ($200\mu\text{eq/mL}$) is greater than that of SU-10 ($70\mu\text{eq/mL}$). The difference of the amount adsorbed between paraquat and diquat from water could be explained by the difference of cation exchange capacity.

The adsorption removal of paraquat and diquat onto C-10 was strongly inhibited by saline more than SU-10. Paraquat, diquat and sodium chloride are ionic and these substances dissociates perfectly in the solution. Chitosan derivatives used are also cation exchanger. It is predicted that the competitions between paraquat, diquat and sodium cation onto adsorption sites occur in the solution. The degree of inhibitory effect in physiological saline solution may be depended to the selectivity of cations to hydrophilic functional group of chitosan derivatives.

It was concluded that the use of chitosan derivatives which having large cation exchange capacity and from sodium chloride free solution was suitable for paraquat and diquat removal.

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