原　著

殺菌剤オキシン銅のキトサン誘導体への吸着

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Adsorption of oxine copper as a germicide onto chitosan derivatives

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要約

ゴルフ場からの排水による飲料水汚染防止を指向して、数種キトサン誘導体による殺菌剤オキシン銅の吸着特性について基礎的検討を試みた。使用したキトサン誘導体のうち、キレートタイプのものがイオン交換タイプのものより、オキシン銅の吸着量、吸着速度いずれにおいても優れていた。ゴルフ場において大量に使用される農薬のうち殺菌剤として繁用されているオキシン銅を含有する排水による飲料水汚染を未然に防止するためには、キレートタイプのキトサンが良好な吸着剤として使用可能であろうことが示唆された。

（臨床環境７：27～31，1998）

Abstract

The adsorption of oxine copper, which is used as a germicide, onto chitosan derivatives was investigated for the treatment of waste water from golf-yards. Concerning chitosan derivatives, the amount of oxine copper adsorbed and the adsorption rate onto chelate resin type of chitosan was significant compared to that of chitosan that was a cation exchanger type. It was suggested that the chelate resin type of chitosan might be an useful adsorbent for the prevention of water pollution by oxine copper as a germicide.

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《Key words》chitosan derivatives, oxine copper, chelate resin type, water pollution

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I. Introduction

In Japan, the environmental destruction caused by the development of golf-yards has advanced rapidly[1]. A significant amount of agricultural chemicals have been applied to golf-yards, and the water pollution by their effusion into ground or river water has been serious problems[2].

Generally, the use of agricultural chemicals is regulated by the agricultural chemicals control law. However, this regulation only concerned agricultural chemicals that were used on farmlands. In May of 1990, the provisional standard of water quality was set up by Ministry of Welfare in Japan[3,4]. Therefore, studies on the removal of agricultural chemicals from water has just started[5].

On the other hand, the shell of *Crustacea* such as crab and lobster had been considered as food waste. The shell of *Crustacea* contains a significant quantity of chitin, β-(1-4) poly-N-acetyl-D-glucosamine. Chitin is the second most produced natural polymer after cellulose[6,7].

In recent years, the research and development on the use of chitin and chitosan, which is deacetylated chitin, has increased. Artificial skin and sutures for surgical operations at medical field are typical examples[8]. However, there are only a few report on the application of chitin and/or chitosan for the preservation in water environment has been done so far[9,10].

In this investigation, we choose oxine copper as a germicide, because its use is common and its toxicity to fish is marked, and we characterized the adsorption of oxine copper onto chitosan derivatives for waste water treatment from golf-yards.

II. Materials and Methods

Oxine copper was obtained as a commercial preparation from Nissan Chemical Industry Co. Ltd. and its concentration was indicated as 80% of copper (II) 8-quinolinolate. Six chitosan derivatives (BCW, SU, CM, CL, CT, and CS) were obtained from Fuji Spinning Co. Ltd. and their properties are shown in Table 1. The particle size was 0.3 mm.

Adsorption isotherms were obtained for the oxine copper solution/chitosan derivatives system. In less than 24 hours, equilibrium adsorption at 25℃ was manifested using constant shaking by a water bath shaker (Iwaki SHK-151B). After equilibration, the copper concentration in the supernatant solution was measured using an atomic absorption spectrophotometer (Hitachi Z-9000).

The time course of oxine copper adsorption was measured at 25℃. One gram of chitosan derivative was placed in a stirred solution of 100 ml of oxine copper solution, which was at a concentration of 100mg/liter of copper. One milliliter of the suspension was sampled at regular intervals, and then the copper concentration was determined.

Table 1 Properties of Chitosan Derivatives.

Chitosan Derivatives	Type	Functional Group (Chelate Group)	Ion Exchange Capacity (mEq/ml)	Surface Area (m^2/g)
BCW	carrier for enzyme immobilization	aromatic alkyl group	0.2−0.3	150−200
SU	cation exchanger	sulfonic group	0.07	70−100
CM	cation exchanger	carboxymethy group	0.20	70−100
CL	chelate resin	iminodiacetic acid	0.83	70−100
CT	chelate resin	aromatic carboxylic acid	1.20	70−100
CS	chelate resin	primary and secondary amine	1.56	70−100

This data is from a technical report by Fuji Spinning Co.Ltd.

Ⅲ. Results and Discussion

Adsorption isotherms of oxine-copper onto chitosan derivatives at 25℃ are shown in Figure 1. The logarithm of the amount adsorbed was plotted linearly against the logarithm of the equilibrium concentration. The linear relationship indicated that the adsorption of oxine copper onto chitosan derivatives was of the Freundlich type[11]. The Freundlich equation is expressed as the following form,

$$\log V = 1/n \log C + \log k$$

where V is the amount adsorbed, C is the equilibrium concentration, and n and k are constants. CL and BCW adsorbed the largest amount of oxine copper and the smallest amount, respectively, over the whole range of less than 1000mg/liter of equilibrium concentration. The amount of oxine copper adsorbed onto the chitosan derivatives for the equilibrium concentrations is shown in Table 2. The amount adsorbed onto the chitosan derivatives was successively larger in the order of CL>CS>CT>CM>SU>BCW. Whole range of below 1000mg/liter of equilibrium concentration, the amount adsorbed onto CL was the largest, and the amount adsorbed at each equilibrium concentration was about 80(at 1mg/liter), 50(at 10mg/liter), 30(at 100mg/liter), or 20(at 1000mg/liter) times larger than that onto BCW, respectively.

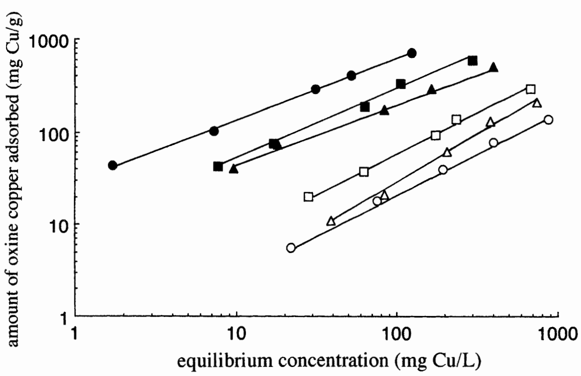

Fig.1 Adsorption isotherm of oxine copper onto chitosan derivatives at 25℃.
○ : BCW, △ : SU, □ : CM, ● : CL, ▲ : CT, ■ : CS
volume of oxine copper solution:100mL, weight of chitosan derivative:1.0g, shaking time:24hours.

Table 2 Amount of Oxine Copper Adsorbed onto Chitosan Derivatives at Equilibrium.

Chitosan Derivatives	Amount of Oxine Copper Adsorbed (mg Cu/g) V at 1mg/L	V at 10mg/L	V at 100mg/L	V at 1000mg/L
BCW	0.39	2.92	21.68	160.98
SU	0.23	2.56	28.03	306.58
CM	1.14	8.16	58.45	418.97
CL	29.65	134.41	609.22	2761.33
CT	9.74	44.29	201.35	915.47
CS	9.71	51.65	274.75	1641.70

The amount of oxine copper adsorbed onto chitosan derivatives was calculated using the Freundlich equation with the data of adsorption isotherm at equilibrium.
V : amount adsorbed (mg Cu/g) at each equilibrium concentration.

The amount of chitosan needed for 90% removal of oxine copper is shown in Table3. The amount of chitosan was calculated according to the method of Ogino *et al*[12]. The equation can be expressed in the following form,

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

where M is the amount of chitosan derivatives needed for 90% removal, C_1 is the initial concentration, C_2 is one-tenth of the concentration of C_1, and V is the amount adsorbed at C_2. For the initial concentrations,

Table 3 Calculated Amount of Chitosan Derivatives needed for 90% Removal of Oxine Copper at Various Initial Concentrations.

Chitosan Derivatives	Amount of Chitosan (g/L) 1000mg Cu/L	100mg Cu/L	10mg Cu/L
BCW	41.52	30.83	22.90
SU	32.11	35.13	38.46
CM	15.40	11.04	7.91
CL	1.48	0.67	0.30
CT	4.47	2.03	0.92
CS	3.28	1.74	0.93

Amount of chitosan derivatives was calculated using the following equation with the data of adsorption isotherms. $M=[C_1-C_2]/V$; M(g/L): amount of chitosan derivatives needed for 90% removal, C_1(mg Cu/L): initial concentration, C_2(mg Cu/L): one-tenth concentration of C_1, V(mg Cu/g): amount of oxine copper adsorbed at C_2.

the amount of CL necessary for 90% removal was less than that of BCW. Considering the amount adsorbed, the chitosan derivatives of chelate resin type (CL, CS and CT) were the most useful adsorbent for oxine copper adsorption.

To characterize the chelate resin, the adsorption rate should be determined. The time dependent adsorption of oxine copper is shown in Figure 2. For CL, the oxine copper concentration was significantly lowered within 20 minutes, and the concentration continued to lower. In CS and CT, the changes were similar to that of CL. The change in oxine copper concentration with SU and BCW were not significant.

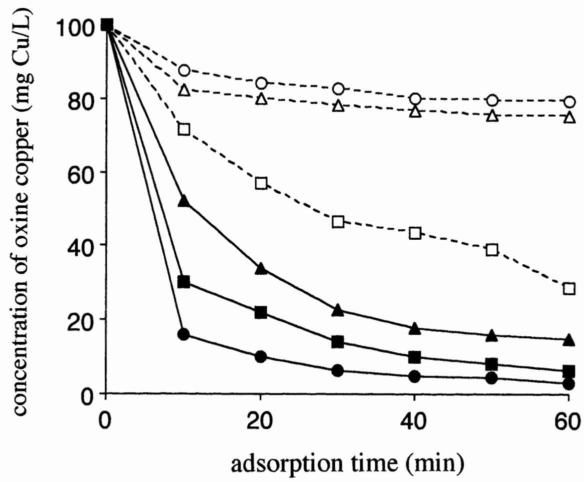

Fig.2 Time dependent adsorption of oxine copper at 25℃.
○ : BCW, △ : SU, □ : CM, ● : CL, ▲ : CT, ■ : CS
volume of oxine copper solution : 100mL, initial concentration : 100mg Cu/L, weight of chitosan derivative : 1.0g, stirring condition : 300rpm.

The the kinetic constant was calculated to elucidate the adsorption rate using the formula of the first-order reaction. The kinetic constant is the absolute value of the slope of the regression line used in the formula of the first-order reaction. Table 4 shows the kinetic constant of oxine copper removal by chitosan derivatives. The kinetic constant for chitosan derivatives was successively larger in the order of CL>CS>CT>CM>SU>BCW. The order of the kinetic constant for chitosan derivatives was the same as that of the amount adsorbed. The kinetic constant of CL was the largest, and it was 14 times larger than that of BCW, which can immobilize enzymes.

Table 4 Kinetic Constant of Oxine Copper Removal by Chitosan Derivatives.

Chitosan Derivatives	Kinetic Constant k (min^{-1}×10^{-3})	Chitosan Derivatives	Kinetic Constant k (min^{-1}×10^{-3})
BCW	0.48	CL	6.69
SU	0.34	CT	5.08
CM	3.30	CS	5.34

Kinetic constant was calculated from the time dependent adsorption of oxine copper onto chitosan derivatives using the formula of the first-order reaction.

In this investigation, we have demonstrated the use of chitosan derivatives to remove oxine copper as a germicide. It has been suggested that some chitosan derivatives might be an useful adsorbent to prevent water pollution caused by waste water containing oxine copper from golf-yards. The chitosan derivatives, which adsorbed the largest amount of oxine copper at the highest adsorption rates were chelate resins. It was found that chitosan derivative as a chelate resin was more useful than other chitosan derivatives as cation exchangers for the adsorption removal of oxine copper.

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