MODIFICATION OF CELLULOSE MATERIALS BY ANTISEPTICS AND THEIR ANTIMICROBIAL PROPERTIES(Ⅱ)*

——Release of antiseptics from modified cellulose materials and their antimicrobial activity

KOTELNIKOVA N E　HOU Y F

KOTELNIKOVA N E[1], HOU Yong-fa[2], PANARIN E F[1], KUDINA N P[1], LI Shu-xiu[2], ZAIKINA N A[3]

(1. Institute of Macromolecular Compound, RAS St. Petersburg 199004, *Russia; 2. Research Institute of Chemical Processing and Utilization of Forest Products, CAF, Nanjing* 210042, *China;* 3. *Chemico-pharmaceutical Institute, St. Petersburg* 197198, *Russia)*

Abstract: Dressing cellulose materials(CM) and bleached cotton cloth (CC) modified by surfactant antiseptics(CA) have been prepared by the method of adsorption interaction between CM and CA. Antiseptics release was studied by the method of desorption in solutions at different pH values. Maximum release of surfactants is achieved in solutions at pH = 7.0. Microbiological tests of modified cellulose materials have shown that they exhibit antimicrobial activity. These results are valuable for practical application in clinics for imparting antimicrobial properties to dressing materials.

Key words: cellulose materials; surfactant antiseptics

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This paper continues a set of our study on adsorption-desorption interaction between cellulose materials and biologically active compounds(BAC) and on the properties of the resulting compounds[1~5]. Adsorption interaction of cellulose materials with surfactant antiseptics have previously been studied[6]. These antiseptics are a complex of the copolymer of N-vinylpyrrolidone and crotonic acid with dimethylbenzylalkylammonium chloride (CVCD) and its low molecular weight analogue dimethylbenzyl-alkylammonium chloride(DMBAA). This paper is devoted to determination of surfactants release from modified cellulose materials by the method of desorption of adsorbed antiseptics into solutions at different pH. Microbiological tests of CM adsorbates have been also studied.

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作者简介:KOTELNIKOVA N E(1942-),女,俄罗斯人,化学博士,研究员。

1 Experimental

1.1 Materials

Modified dressing materials and cotton cloth have been prepared as described in [6].

1.2 Methods

Desorption of the resulting samples was carried out as follows: 0.3~1.0 g sample feed was placed in phosphate buffer solutions (mass ratio 1∶60) at pH 5.0, 7.0 and 8.0 at room temperature for 2 h.

Determination of antimicrobial activity was carried out[7] by diffusion into agar with respect to the following strains of microorganisms: gram-positive *Staphylococcus aureus* 16 and *Bacillus subtilis*, gramnegative *Escherichia coli* and *Preudomonas aeruginosa*. Samples 1 cm^2 and 0.25 cm^2 in size were spotted on agar surface sown with grass and the zone of growth decrease around them was marked. Experimental details and calculation procedure have been reported in [7].

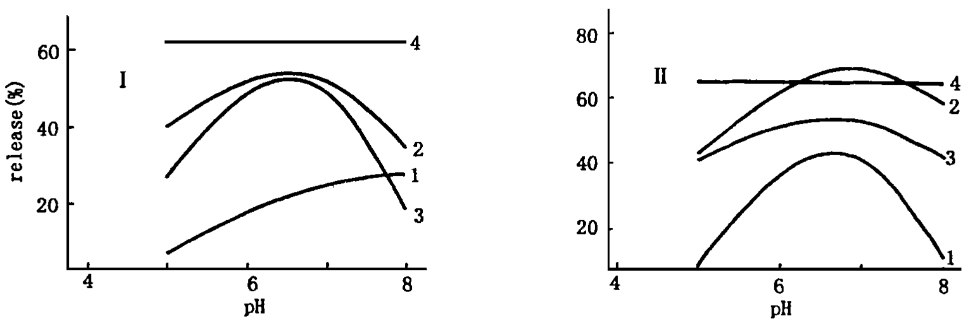

Fig. 1 Dependences of release of adsorbed DMBAA (Ⅰ) and CVCD (Ⅱ) from modified DM samples (1, 2) and CC samples (3, 4) into solution on the pH of these solutions

DMBAA content in the samples after adsorption: 1. 94 mg/g; 2. 309 mg/g; 3. 54 mg/g; 4. 232 mg/g;

CVCD content in the samples after adsorption: 1. 76 mg/g, 2. 330 mg/g, 3. 76 mg/g, 4. 380 mg/g.

2 Results and discussions

The ability of samples obtained as a results of adsorption to emit a biologically active adsorptive into the environment determines their properties as BAC in practical application. Fig. 1 shows the dependence of DMBAA (Ⅰ) and CVCD (Ⅱ) adsorption from CC and DM in solutions on the pH of these solutions. It is clear that in the case of CC and DM modified by DMBAA, desorption increases with adsorption value (AV). The only exceptions are experiments on DMBAA and CVCD desorption from CC samples obtained by adsorption from solutions of maximum concentration equal to 100 mg/mL. In this case desorption is maximum, does not depend on pH and is on the average 61%~64% (mass) of the adsorbed amount. In all other cases maximum desorption value is at pH 7. A similar dependence in the range of pH investigated is observed for both cotton MCC and other types of MCC of different natural origins[5,7]. Therefore, these relationships are common for both different cellulose types and CM.

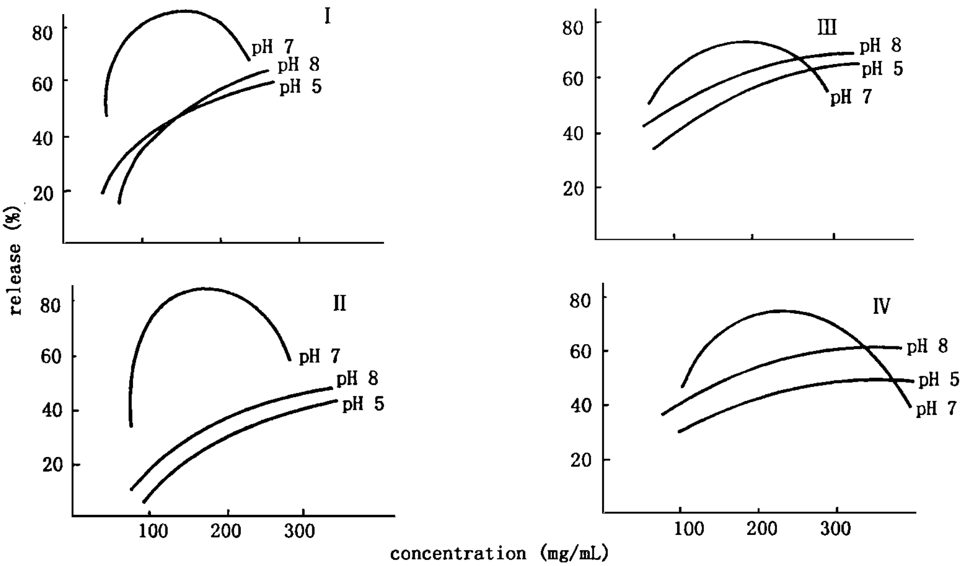

Fig. 2　Desorption isotherms of DMBAA(I , II) and CVCD(III, IV) from modified CC (I , III) and DM (II , IV) samples into solutions with different pH values

Fig. 2 (I ~ IV) shows desorption isotherms of adsorptives from CC(I and II) and DM(III~ IV) samples. It can be seen that when CC is used as adsorbent, the dependence of the quantity of adsorptives passing into solution at pH 5 and 8 on their quantity in the adsorbent has the shape of a limit hyperbola but does not attain the limit in this concentration range. The quantity of undesorbed adsorptive increases with its concentration in the adsorbent. Thus, the quantity of CVCD undesorbed from CC is approximately the same 45~ 50 mg/ g (at low AV) and 110~ 120 mg/ g (at high AV), regardless of the pH of solutions used for desorption. In the case of DMBAA these values are 45 ~ 50 and 95~ 105, respectively. When adsorptives pass into solutions at pH 7, this dependence is of the extreme character at maximum DMBAA (85% ~ 87%, mass) and CVCD(75%, mass) desorption at this concentration in the samples of 150~ 200 mg/ g. In this case the quantity of undesorbed DMBAA is 20 mg/ g and that of CVCD is 50 mg/g. A similar dependence is observed when DM(III, IV) is used as adsorbent. However, the quantity of undesorbed DMBAA in desorption into solutions at pH 5 and 8 is higher than in the case of using CC and is 60~ 80 mg/ g at low DMBAA concentrations in DM and 135 ~ 165 mg/ g at its high concentrations. In the case of CVCD these values are 45~ 50 and 80% (mass), respectively. At maximum desorption in solution at pH 7(85%) the amount of undesorbed DMBAA is 25 mg/ g and that of CVCD (75%) is 60 mg/ g. It is evident that data on incomplete desorption of 1 and 2 agree with our conclusion that chemical interaction takes place between CM and DMBAA and CVCD.

The difference in adsorption and desorption processes is probably explained by the fact that the materials investigated differ in texture and contain natural pores which are evidently responsible for the diffusion stage of adsorption and desorption. In this connection differential curves of numerical pore sizes distribution were plotted. Pore number was calculated with the aid of a polarizing microscope with a screw ocular micrometer (ERGAVAL microscope, Carl Zeiss, Yena) Fig. 3 shows the results. It can be seen that the area of most pores (70%) of CC ranges from 15 ~ 30·10^2 mm^2 (Ⅰ) and that of DM from 70 ~ 90·10^2 mm^2 (Ⅱ). Note that the maximum AV of DMBAA and CVCD are higher for DM, which is in agreement with the size of natural DM pores. These pores are 3 ~ 5 times higher than that for CC.

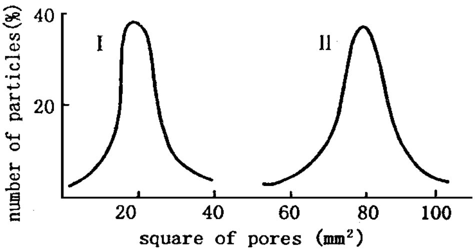

Fig. 3 Differential curves of pore size distribution for CC (Ⅰ) and DM (Ⅱ) initial samples.

Table 1 Antimicrobial activity of modified cellulose materials with respect to strains

samples	DMBAA (Ⅰ) and CVCD (Ⅱ) concn. in the sample (mg/g)		zone of growth arrest (mm)					
			Escherichia coli		*Bacillus subtilis*		*Pseudonmonas aeruginosa*	
	Ⅰ	Ⅱ	DMBAA	CVCD	DMBAA	CVCD	DMBAA	CVCD
cotton cloth	5.1	8.1	32	30	35	38	32	30
	3.2	4.7	27	28	30	32	27	28
dressing material	1.9	6.6	30	25	30	35	30	25
	1.3	1.7	28	25	28	30	28	25

Table 2 Antimicrobial activity of cellulose materials with respect to strains of *Staphylococcus aureus* 16

cellulose materials	sample size (cm^2)	DMBAA (Ⅰ) and CVCD (Ⅱ) concn. in the sample (mg/g)		zone of growth arrest of the test microbe (mm) in the sample containing		concn. of DMBAA and CVCD isolated during the biotest (mg/g)		desorption value of DMBAA and CVCD in water (%)		desorption value according to biotest (%)	
		Ⅰ	Ⅱ	DMBAA	CVCD	DMBAA	CVCD	DMBAA	CVCD	DMBAA	CVCD
cotton cloth	1	5.1	8.1	32	32	1.9	5.6	65.0	63.3	57.2	69.1
	0.25	3.2	4.7	31	32	1.8	5.6	63.0	74.6	56.2	79.1
dressing material	1	1.9	6.6	33	35	2.3	10.0	56.0	82	47.9	85
	0.25	1.3	1.7	32	33	1.9	6.3	73	77	68.0	79

Tables 1 and 2 give the results of microbiological tests of CM adsorbates. Each sample gives the zone of growth arrest of the strains. The diameter of this zone is in agreement with the size of the sample. It is of interest that modified CM suppresses the development of both gram-positive and gram-negative pathogenic microorganisms. This confirms the promising possibility of preparation of antiseptic CM with the application of DMBAA and CVCD for medical purposes. To establish correlation between the activity of CM modified by antiseptics and the diameter of the arrest zone in the case when *Staphylococcus aureus* 16 was used, calibration dependences which had been previously established were applied[1]. The results of calculations (Table 2) show that the quantity of DMBAA diffusing into agar is slightly less than that passing into water as a result of desorption at pH 7, whereas the quantity of CVCD diffusing into agar is essentially within the same range as that diffusing into water during desorption. Earlier it has been shown that DMBAA can be bound to cellulose more strongly than CVCD[7].

Hence, these data confirm the previous results. It is noteworthy that during desorption carried out with excess solvent (in this case, water) and in microbiological tests performed by diffusion into agar under the conditions of limited swelling because of water lack, the results of determination of the amounts of released substances are very close to each other. This fact indicates that the intensity of BAC release is very high and emphasizes again that the use of CM modified by antiseptics is very promising.

Consequently, as a result of this study, the relationships of DMBAA and CVCD adsorption on cellulose materials and adsorbates desorption were established. Microbiological tests of CM modified by antiseptics have shown that modified CM exhibit antimicrobial activity. These results can be used in medical practice in clinics for imparting antimicrobial properties to dressing materials.

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抗菌剂改性纤维素物料及其抗菌性能(Ⅱ)
——改性纤维素物料抗菌素的释出及其抗菌性能

柯捷里尼科娃 N E[1], 侯永发[2], 帕纳林 E F[1], 库吉娜 N P[1],
李淑秀[2], 扎伊金娜 N A[3]

(1. 俄罗斯科学院高分子化合物研究所, 圣彼得堡市 199004; 2. 中国林业科学研究院林产化学工业研究所, 江苏 南京 210042; 3. 国立圣彼得堡药科大学, 圣彼得堡市 197198)

摘　要: 抗菌剂(CA)改性棉纱布(CM)和漂白棉布(CC)系经 CA 与 CM 和 CC 相互吸附作用而制成。本文研究了在不同 pH 值溶液中抗菌素释出状况。试验结果证明, 在 pH = 7.0 时抗菌素释出量最大。改性纤维素物料的微生物试验表明其具有抗菌性能, 作为重要医疗包扎物品, 具有实际应用价值。

关键词: 纤维素物料; 表面活性抗菌剂