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The Usage of Copper Modified Natural Zeolites in Textile Finishing as an Antibacterial Agent

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Abstract—**Natural zeolites are one of the most examined natural minerals. By means of new studies conducted on zeolites, new areas of use are being discovered day by day. It is possible to produce modified zeolites having many variable functions by using the ion exchange capability of zeolite. The characteristics of the cotton fabrics treated with copper-loaded antibacterial zeolite are analyzed in this article.**

Keywords—zeolite, copper, antibacterial, textile, ICP-MS

I. Introduction

Zeolite is a mineral group with hydrated alumina silicate composition including alkali and alkaline-earth cations chemically in its framework silicate structure. There are channels and gaps, the sizes of which differentiate between 3-10 angstrom, within their structures. The main units within the zeolite structure are SiO_4 and AlO_4 tetrahedra where Si and Al, which can be replaced by Si, are located in the center [1]. The order composed by tetrahedra in zeolites, cations and water molecules form a general zeolite chemistry as **"(Na, K, Li, Ca, Mg, Fe, Ba, Sr) $(Al\ Si_{2\text{-}5})_{6\text{-}12}\ O_{12\text{-}24} \cdot nH_2O$".** The ideal zeolite chemistry hosts as many cations as Al that replaces Si. Cations within the pores of zeolites are dynamic and they can be replaced by the cations in the solutions when it contacts with the solutions including other cations [1,2]. The ion exchange observed in the zeolites takes place in accordance with the reaction given below:

$$A^{+} + BZ \rightleftharpoons B^{+} + AZ \qquad (1)$$

In this reaction, a solution including A ions is contacted with a zeolite carrying B ions, and the A ions in the solution are replaced by the B ions in the zeolite [1].

There are some studies regarding the use of zeolites functionalized through ion exchange in the textile and leather industry. Japanese researchers produced antibacterial artificial leather using antibacterial zeolite [3]. Yoshikazu et al. produced antibacterial recycled polypropylene [4]. Taisheng et al. produced antibacterial shoe lining [5]. Ruiwen et al. succeeded in producing antibacterial viscose fiber [6]. Bozoğlu produced antibacterial diapers with silver and zinc ion exchanged zeolite. He reported that he achieved good results against E.Coli; however he experienced some problems regarding color change [1]. In this study, some features such as antibacterial efficiency, washing durability, change of whiteness degree by applying the copper loaded zeolites on the cotton fabric at different concentrations. The study will contribute to the literature with respect to the medical areas of use of cotton fabrics treated with copper-loaded zeolite. Following the silver, copper is one of the commonly used metals in the textile production. By using the zeolite as a copper ion carrier, copper ions are released into the environment slowly and at low concentrations, this way both the toxic risk will not be a threat and the antibacterial efficiency will last longer. In the wake of the study results, it is thought that the textile products including Cu-Na-zeolite can be used as wound dress.

II. Material and Method

The fabric used in the trials was a 100% cotton, de-sized, scoured and bleached woven textile fabric. The natural zeolite used in the trials was provided from Enli Madencilik A.Ş. and belongs to the Manisa - Gördes region; its grain size is 30 µm.

By loading the natural zeolite with Na^+, Na-zeolite was obtained. NaCl was used as the Na^+ source. The natural zeolite was treated in 1 N NaCI solution with a mixing speed of 500 rpm at 60 °C in a glass beaker for 1 week during the process. NaCI solution was replaced each day. After this process, the sample was thoroughly washed with purified water for several times and dried at 110°C in drying oven. The main purpose of this treatment is to purify the natural zeolite from other elements in its structure and increase its cation binding capacity. The Na-zeolite obtained was treated in the following solution (0.1 M and 0.01 M) $Cu(NO_3)_2.6H_2O$ at two different concentration levels in a magnetic mixer (with a mixing speed of 500 rpm) for two days at room temperature. After the modification treatment, the modified zeolites were washed with purified water for five times and dried at 110°C in the drying oven; this way Na-Cu-zeolite was acquired. Na-Cu-zeolite was applied on the cotton fabric by means of a acrylic based binder at three different concentration levels (5 g/l, 1.25 g/l and 0.3125 g/l both 0.1 M and 0.01 M). Padding recipe is a modified pigment dyeing recipe. The pick-up values were approximately 80 %.

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Wetting Agent (g/l) : 5
Thickener (g/l) : 20
Binder (g/l) : 5
pH : 7
Pick-up Value (%) : 80
Zeolite (g/l) : 0.3125, 1.25, 5
Application Condition: Room temperature
Drying : 110 °C 4 minutes

FİGURE 1. Application Recipe

III. Results and Disscussions

The copper ion amount on the cotton fabric was measured with ICP-MS (Inductively coupled plasma mass spectrometry) (Agilent ICPMS 7500ce). Before the measurement process was performed with ICP-MS, the cotton fabrics treated with Na-Cu-zeolite were carbonized within acid solution (HNO_3 and HCl) in the microwave oven (MARS Microwave Accelerated Reaction System MARS 5 Version 194AO2). Thereafter, elemental analysis was carried out.

TABLE 1.Cu Ion Content of the Cotton Fabrics (ICP-MS)

Treated Cotton Fabrics	**Zeolite Modified by 0.1M $Cu(NO_3)_2.21/2H_2O$**		**Zeolite Modified by 0.01M $Cu(NO_3)_2.21/2H_2O$**	
	Cu ion content (mg)/ Fabric Quantity (10g)		**Cu ion content (mg)/ Fabric Quantity (10g)**	
	Unwashed	**20 Times Washed**	**Unwashed**	**20 Times Washed**
5 g/l Na-Cu-Zeolite	0.746	0.051	0.356	0.038
1,25 g/l Na-Cu-Zeolite	0.287	0.036	0.097	0.016
0,3125 g/l Na-Cu-Zeolite	0.059	0.015	0.058	0.011

When the table 1 is considered, it is seen that the Cu ion amounts on the fabrics (treated with 0,1 M Cu-Na-Zeolite) are 0.746, 0.287 and 0.059 mg/10 g fabric, respectively. After the 20^{th} washing process, these values went down to 0.051, 0.036 and 0.015 mg/10 g fabric, respectively. Also, when the table 1 is considered, it is seen that the Cu ion amounts on the fabrics (treated with 0.01 M Cu-Na-Zeolite) are as follows: 0.356, 0.097 and 0.058 mg/10 g fabric, respectively. After the 20^{th} washing process, these values went down to 0.038, 0.016 and 0.011 mg/10 g fabric. These results indicate that the Cu ion amount on the fabric is directly proportional to Cu ion amount within the application solution; also that the Cu ion amount went down significantly after the washing processes. Both analysis values measured before and after the washing processes seem very consistent.There is a significant difference between the Zn ion amounts on the cotton fabrics treated with 0.1 M and 0.01 M Zn-Na-Zeolites equally.

The antibacterial efficiency tests were conducted in accordance with AATCC 100. Gram-positive *S.Aureus* (AATCC 6538) and gram-negative *K.Pneumoniae* (AATCC 4352) were used in the tests. Washing durability tests were performed following the 5th, 10th, 15th, and 20th washing processes. The washing processes took place in the lab-type dyeing machine using ECE (SDL Atlas reference detergent B) at 60 °C. Wascator or household washing machine was not used during the washing process due to the contamination risk.

TABLE 2. Washing Durability and Antibacteraial Properties of the Treated Fabrics

Treated Cotton Fabric with 5 g/l of Zeolite Modified by $Cu(NO_3)_2.21/2H_2O$				
Washing Cycles	**0.1 M**		**0.01 M**	
	S.Aureus	***K.Pneumoniae***	***S.Aureus***	***K.Pneumoniae***
	Reduction (%)	**Reduction (%)**	**Reduction (%)**	**Reduction (%)**
Unwashed	75.03	62.85	69.35	47,93
5	58.955	46.99	43.19	35.055
10	29.905	20.665	17.655	16,73
15	8.185	2.70	2.37	0
20	1.85	1.385	0	0

(*) The antibacterial efficiency tests were repeated twice. The test result was assessed considering the total number of bacteria on the cotton fabric, which is 4.8 cm in diameter. At the beginning of the test, 10^8 cfu/ml bacteria was cultivated on the fabric, the diameter of which is 4,8 cm. The number of bacteria at 0.time compared with the number of the bacteria at the end of the 6 hours. And % reduction was calculated

As it is seen on the table 2, the antibacterial efficiency of the sample that was treated with 0.1 M 5 g/l and was not washed was around 75.03 % against gram-positive *S.Aureus*, and around 62.85 % against gram-negative *K. Pneumoniae* at the end of 6 hours*;* after the 20th washing process it was observed that these values went down to app.1.85 % against gram-positive *S.Aureus,* and to app.1.385 % against gram-negative *K. Pneumoniae*. Also, as it is seen on the table 2, the antibacterial efficiency of the sample that was treated with 0.01 M 5 g/l and was not washed was around 69.35% against gram-positive *S.Aureus*, and around 47.93 % against gram-negative *K. Pneumoniae* at the end of 6 hours*;* after the 20th washing process it was observed that these values went down to app. 0 % against gram-positive *S.Aureus*, and to 0 % against gram-negative *K. Pneumoniae*. As the number of washing process increased and the copper amount decreased, the number of bacteria to survive increases.

TABLE 3. Washing durability and Antibacteraial properties of the treated fabrics

Treated Cotton Fabric with 1.25 g/l of Zeolite Modified by $Cu(NO_3)_2.21/2H_2O$				
Washing Cycles	0.1 M		0.01 M	
	S.Aureus	*K.Pneumoniae*	*S.Aureus*	*K.Pneumoniae*
	Reduction (%)	Reduction (%)	Reduction (%)	Reduction (%)
Unwashed	55.255	47.46	46.65	46.07
5	30.865	18.115	17.255	13.09
10	12.68	13.695	7.925	10.225
15	3.125	4.895	1.11	0
20	0	0	0	0

As it is on the table 3, the antibacterial efficiency of the sample that was treated with 0.1 M 1.25 g/l and was not washed was around 55.255% against gram-positive *S.Aureus*, and around 47.46 % against gram-negative *K. Pneumoniae* at the end of 6 hours; after the 15th washing process it was observed that these values went down to app.3.125 % against gram-positive *S.Aureus*, and to 4.895 % against gram-negative *K. Pneumoniae*. This indicates that the copper ion amount on the fabric is not sufficient enough to create antibacterial effect. As it is seen on the chart 3, the antibacterial efficiency of the sample that was treated with 0.01 M 1.25 g/l and was not washed was around 46.65% against gram-positive, and around 46.07% against gram-negative *K. Pneumoniae* at the end of 6 hours; after the 15th washing process it was observed that these values went down to app.1.11% against gram-positive *S.Aureus*, and to 0% against gram-negative *K. Pneumoniae.*

TABLE 4. Washing durability and Antibacteraial properties of the treated fabrics

Treated Cotton Fabric with 0.3125 g/l of Zeolite Modified by $Cu(NO_3)_2.21/2H_2O$				
Washing Cycles	0.1 M		0.01 M	
	S.Aureus	*K.Pneumoniae*	*S.Aureus*	*K.Pneumoniae*
	Reduction (%)	Reduction (%)	Reduction (%)	Reduction (%)
Unwashed	21.765	32.045	13.7	19.03
5	14.21	17.09	3.91	4.765
10	4.91	4.295	0	0
15	0	0	0	0
20	0	0	0	0

As it is on the table 4, the antibacterial efficiency of the sample that was treated with 0.1 M 0.3125 g/l and was not washed was around 21.765% against gram-positive *S.Aureus*, and around 32.045% against gram-negative *K. Pneumoniae* at the end of 6 hours; after the 10th washing process it was observed that these values went down to app.4.91% against gram-positive *S.Aureus*, and to 4.295% against gram-negative *K. Pneumoniae*. As it is seen on the chart 3, the antibacterial efficiency of the sample that was treated with 0.01 M 0.3125 and was not washed was around 13.7% against gram-positive, and around 19.03% against gram-negative *K. Pneumoniae* at the end of 6 hours; after the 10th washing process it was observed that these values went down to app.0% against gram-positive *S.Aureus*, and to 0% against gram-negative *K. Pneumoniae.*

The whiteness degrees of the fabrics were measured with spectrophotometer (Minolta CM-3600 d) according to the Stensby Formula.

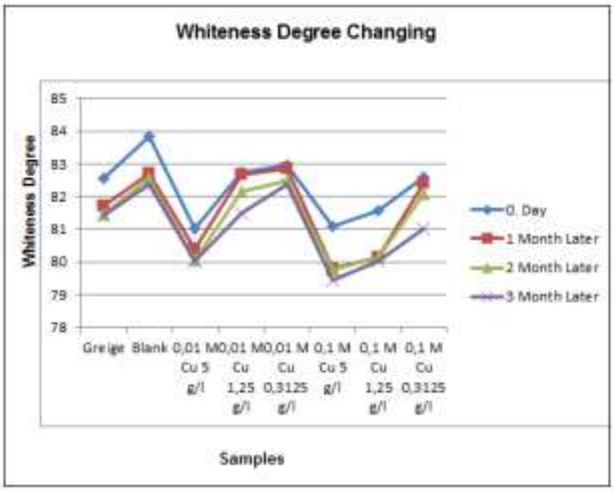

FİGURE 2. Whiteness Degree Changing

Analyzing the Figure 2, it is seen that the whiteness degree of the greige fabric is lower than the blank fabric's (blind fabric is a fabric treated with an application solution including no Cu-Na-zeolite). The application solution is considered as the reason why the whiteness degree of the untreated fabric is lower than the blank fabric. Because the thickener and the binder which were used in application solution are white. It is clearly seen that as the Cu ion and zeolite amount on the fabrics increased, the whiteness degree of the fabric decreased. The reason of this is colour of zeolite. The whiteness degree of the cotton fabrics treated with Cu-Na-Zeolite concentrated in 0.1M is lower than the cotton fabrics treated with Cu-Na-Zeolite concentrated in 0.01 M. This indicated the effect of the concentration.

IV. Conclusion

The natural zeolite was modified with Cu(NO3)2.21/2H2O and Cu-Na-Zeolite was obtained in this study. The copper ion amounts loaded to the natural zeolite were measured with ICP-MS. The Cu-Na-zeolites obtained (0.01 M and 0.1 M) were applied on the cotton fabrics in three different quantities by means of an acrylic based binder and their antibacterial efficiencies along with their washing durability were tested against gram-positive S.Aureus and gram-negative K. Pneumoniae. Depending on the modification concentration and amounts applied on the fabric, different results regarding antibacterial efficiency and washing durability were acquired.

Analyzing the whiteness degrees, it is seen that as the zinc ion amount on the cotton fabric increases, the whiteness degree decreases. However, the decline in the whiteness degree is not a level to affect the usability of the fabric.

Following the silver, copper is one of the commonly used metals in the textile production. By using the zeolite as a copper ion carrier, copper ions are released into the environment slowly and at low concentrations, this way both the toxic risk will not be a threat and the antibacterial efficiency will last longer [7,8]. In the wake of the study results, it is thought that the textile products including Cu-Na-zeolite can be used as wound dress. This study is a preliminary study carried out on the antibacterial activities of copper charged zeolites. Therefore, studies can be performed with textile materials other than cotton fabric along with the optimization works in the future, and product can be developed for each product and field where antibacterial activity is required like wound dress.

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