Superhydrophobic textile: treatment in aqueous solutions of aluminum salts

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Research Article

Abstract

Textile is currently a promising material. Obtaining hydrophobic surfaces on textiles significantly increases its value when used in various fields. In this work we carried out experiments on textile processing. Treatment of textile materials in solutions containing aluminum allows to obtain a superhydrophobic surface. $KAl(SO_4)$ and $AlCl_3$ solutions were used. It was found that treatment in $AlCl_3$ solution is more effective and allows to achieve a hydrophobic surface on textile with a contact angle of more than 150°. The hydrophobic surface retained its properties even after 30 days. Textile samples were investigated using X-Ray photoelectron spectroscopy (XPS). The X-Ray photoelectron spectroscopy results showed hydrophobicity in the treatment of textile materials is ensured by the formation of aluminum oxide on the surface. The dependence of the coarse calico contact angle on the $AlCl_3$ solution concentration is determined. which demonstrates that when the concentration of $AlCl_3$ solution increases (within the limits of variation considered), the contact angle also increases.

Introduction

Technical textile is widely used in such diverse fields as medical technology, aerospace and automotive industries, modern architecture and building, filtration and transport systems (Holme I. 2007; Çay A. et al. 2020; Karpushko E. N. et al. 2016; Cherston J. and Paradiso J. A. 2019; Thierry V. et al. 2018). To achieve increased hydrophobicity self-cleaning ability and the ability to create barrier coatings on the surface of the fibers, a surface modification of the materials is required.

Nowadays, there are many known methods for modifying the surface of textile materials, these include: treatment in aqueous solutions of various compositions; sol-gel method (Yang M. et al. 2018; Lin D. et al. 2019; Liang J. et al. 2013); methods of deposition nanoparticle to create roughness on surface (Xue C. H. et al. 2008), chemical vapor deposition (CVD) (Şimşek B. and Karaman M. 2020) and plasma-chemical treatment (Gaiolas C. et al. 2013; Pandit P. et al. 2020; Belhaj Khalifa I. and Ladhari N. 2019; Xu L. et al. 2019; Samanta K. K. et al. 2016; Molina R. et al. 2017). The essence of the methods consists of the formation of thin hydrophobic layers on the materials surface (Daoud W. A. et al. 2004) or inoculation of various functional groups that change the surface properties cardinally [18].

Fluorocarbons with subsequent thermal stabilization are most often used as hydrophobizing agents (Bahners T. et al. 2008). As an alternative to fluorocarbons, hydrophobic silicone-based layers are proposed to be obtained.

The paper (Daoud W. A. et al. 2004) describes a method of producing hydrophobic silicon dioxide films of nanometer thickness on cotton fabrics, providing a contact angle of 140°. A significant disadvantage of the method is the high process time, since the preparation of the necessary solutions may take about a day, which significantly affects the total process time.

In (Xue C. H. et al. 2008; Xu L. et al. 2012; Liang J. et al. 2013), the sol-gel method was used to form silicon dioxide coatings from a modified hydrosol of SiO_2, the results of which showed that, compared to untreated samples with a contact angle of 0º, after treatment, the contact angle had reached 152º in the papers (Xu L. et al. 2012; Liang J. et al. 2013), and in (Xue C. H. et al. 2008) contact angle was 145–155º. Even higher contact angles (163⬚) were achieved (Xue C. H. et al. 2008) when using hydrophobic coatings based on TiO_2 being obtained from a TiO_2 sol. The sol-gel method, although it is one of the simplest to obtain thin films, including hydrophobic ones, but its implementation is difficult to obtain a sol, as well as its stabilization. To stabilize the sols, additional reagents are required, which significantly increases the cost of the entire processing process. Another disadvantage of the sol-gel methods is the necessity of repeating certain steps of the production of coatings, which increases the overall process time.

The surface treatment in solutions and emulsions, which include aluminum-containing reagents, is highly effective in achieving the hydrophobicity of various textile materials. One of the main methods of obtaining hydrophobic aluminum-containing coatings is Atomic Layer Deposition (ALD) (Xingfang X. et al. 2015; Hyde G. K., et al. 2010). So, in article (Xingfang X. et al. 2015) aluminum oxide was deposited onto wool fabrics by exposing them to alternating pulses of trimethylaluminum and water at 80°C. The water contact angles of ALD coated wool fabrics increased from 130° to around 160°. The authors of (Hyde G. K., et al. 2010) created aluminum oxide coatings and studied the surface wettability according to the Cassie – Baxter and Wenzel models. They created surfaces with a contact angle about 140º.

Cheaper and simpler than the ALD is the wet chemistry method for obtaining hydrophobic surfaces containing aluminum on textile materials. Despite the simplicity of the method, there is little research that is not aimed at studying the capabilities of the method and various dependencies. Therefore, the researching the possibility of achieving high hydrophobicity of textile materials as a result of their treatment in $KAl(SO_4)$ solution and $AlCl_3$ solution, experimental determination of the effect of treatment parameters on the contact angle, as well as finding out the reasons for the increase surface hydrophobicity.

Materials And Methods

The textile samples were squares of coarse calico with a density of 142 g/m^2 and chintz with a density of 80 g/m^2. The warp and weft fibers are alternately interconnected in a 1:1 pattern. Sample size was (10x10) mm^2. The choice of such a sample size is due to preliminary experiments, which showed that the contact angle under the same processing conditions on samples (10x10) mm^2 and (300x400) mm^2 is identical.

Samples were dipped for 15 minutes in a soap solution with a concentration of 35 g/l and a temperature of 75° C in order to clean the surface from unwanted impurities. We used soap with pH = 7 to make the solution. The concentration of $KAl(SO_4)$ solution and $AlCl_3$ solution was 80 g/l and 35 g/l, respectively. $KAl(SO_4)$ solution was prepared from powder of "h" (GOST 4329-77) 2 class of purity and was diluted

with distilled water to the desired concentration. $AlCl_3$ solution was prepared similarly from $AlCl_3$ powder of the "analytical grade" (GOST 3759-75) purity class.

Resistive heating was used to provide the required temperature of the aqueous solution. Temperature was controlled by a thermocouple. Textile samples were dried using three layers of filter paper, without wringing. After treatment the samples in solutions, they were exposed to the action on an ironing press at a temperature of T = 120 ° C. To maintain constant moisture after treatment, the samples were placed in a desiccator, in which phosphoric anhydride was used as a desiccant.

Wettability control was carried out by measuring the contact angle of wetting using the "sitting" drop method (Vohrer U. et al. 1998; Gao L. et al. 2009; Marmur A. et al. 2017). Error of measuring the contact angle of the surface is 1.5% of the indication. Dosing of the droplet volume was carried out using a Proline® mechanical dispenser with an accuracy of 1.5%. The contact angle was determined using a specialized computer program.

The research of the surface composition of the textile materials after treatment was carried out by X-ray photoelectron spectroscopy on a super-vacuum complex "Nanofab 25" company SPECS. We used Mg Kα radiation with an energy of 1253 eV. The energy linewidth of X-ray radiation without monochromatization was about 0.5 eV. We recorded survey spectra with a step of 1 eV, spectra of individual lines with a step of 0.1 eV.

Results And Discussions

The results of preliminary experiment on the treatment of coarse calico samples in solutions of $AlCl_3$ testified to the achievement of hydrophobization of the treated surfaces (Fig. 1).

It was found that when $KAl(SO_4)$ solution was treated in a solution, the contact angle was less than when processed in $AlCl_3$ solution. Table 1 shows the results of measuring the contact angle. Before the treatment, a drop of water was absorbed instantly on the surfaces of coarse calico and chintz, that means, the surface was completely hydrophilic, and the contact angle can be considered equal to 0⍟.

Table 1
Results of the contact angle measuring

Name of material	Non treatment	$AlCl_3$ solution	$KAl(SO_4)$ solution
Coarse calico	0° ± 1°	160° ± 2°	139° ± 1°
Chintz	0° ± 1°	155° ± 1°	139° ± 1°

Due to the fact that the contact angle on the processed samples of coarse calico and chintz was characterized by the same values, the result of treatment did not depend on the sample material, further studies were carried out on only one material, where coarse calico was used.

To determine the surface composition of the samples obtained during processing in $AlCl_3$ and $KAl(SO_4)$ solutions, we used the method of X-ray photoelectron spectroscopy, the results of which are presented in Fig. 2 and Fig. 3.

For a more correct presentation of the data, the spectral regions with low intensity are enlarged and shown in the footnote in the right corner. The spectra of the processed samples were examined in more detail. In Fig. 3 shows the decomposition of the peak of oxygen (O 1s).

Analyzing of the oxygen peak of the treated samples allowed us to conclude that there are oxygen bonds with carbon, as well as with aluminum, on the coarse calico surface. The bonds with carbon correspond to the composition of the textile material, and the bonds of oxygen with aluminum indicate the presence of aluminum oxide on the surface of the treated samples (Moulder J. 1992). According to the obtained XPS spectra, it can be concluded that the hydrophobicity of coarse calico and chintz is ensured by the formation of alumina on the surface during treatment in solutions of $KAl(SO_4)$ and $AlCl_3$. The experimental results allowed us to conclude that when treatment in a solution of $AlCl_3$ solution, a greater hydrophobicity of the surface is achieved than when treatment in a $KAl(SO_4)$ solution. Therefore, the research of the influence of the processing conditions of the samples on the contact angle was carried out on the example of coarse calico treated in a solution of $AlCl_3$ solution.

The influence of the concentration of soap solution on the contact angle of coarse calico was investigated in the first series of experiments. The temperature of the soap solution, the treatment time in the soap solution, the concentration of the $AlCl_3$ solution, the time of treatment in the $AlCl_3$ solution, and the temperature of thermal exposure were fixed at the following values: 70° C, 25 min, 25 g / l, 25 min, 100° C, respectively. The temperature of $AlCl_3$ solution in all experiments was room temperature (23° C), and the concentration of soap solution in the experiments varied from 15 to 55 g/l. The results of the first series of experiments are presented in Table 2.

Table 2
Results of the first series of experiments

Number of samples	$C_{s.s.}$ = 15 g/l	$C_{s.s.}$ = 35 g/l	$C_{s.s.}$ = 55 g/l
	The contact angle	The contact angle	The contact angle
1	147° ± 1°	148° ± 2°	149° ± 1°
2	148° ± 2°	150° ± 1°	150° ± 2°
3	148° ± 2°	146° ± 1°	147° ± 1°
4	146° ± 2°	148° ± 1°	147° ± 3°

The results of the experiments showed that the concentration of soap solution does not have a strong effect on the contact angle of the coarse calico surface, so in further experiments this parameter was 35 g/l.

In the second series of experiments, the influence of the temperature of a solution of $AlCl_3$ solution on the contact angle of coarse calico was investigated. Temperature (70⬚ C) and the concentration of soap solution (35 g/l), the concentration of $AlCl_3$ solution (25 g/l), the processing time in the soap solution (25 min) and $AlCl_3$ solution (25 min), as well as the temperature of thermal exposure (100° C) were unchanged.

Table 3
Results of the second series of experiments

Number of sample	$T_{AlCl3} = T_{room}$	$T_{AlCl3} = 40°C$	$T_{AlCl3} = 60°C$
	The contact angle	The contact angle	The contact angle
1	147° ± 1°	146° ± 1°	147° ± 1°
2	145° ± 2°	146° ± 1°	146° ± 2°
3	148° ± 1°	146° ± 1°	145° ± 1°
4	145° ± 2°	148° ± 1°	147° ± 1°

Based on the results of the second series of experiments, it was concluded that the temperature of the $AlCl_3$ solution has no strong effect on the treatment result (contact angle of surface). Therefore, subsequent experiments were carried out at a constant temperature of a solution of $AlCl_3$ solution.

Then, the dependence of the contact angle of the coarse calico surface on the concentration of the $AlCl_3$ solution was determined experimentally with fixed values of the temperature of the soap solution, the processing time in the soap solution, the concentration of the $AlCl_3$ solution, the processing time in the $AlCl_3$ solution and the temperature of the thermal effect. The concentration of the $AlCl_3$ solution varied between 15–35 g/l.

The plot of the dependence of the contact angle on the concentration of the $AlCl_3$ solution is shown in Fig. 4.

As can be seen from the obtained graph, with an increase in the concentration of the $AlCl_3$ solution (within the considered variation limits), a slight increase in the contact angle of the coarse calico wetting is observed, nevertheless, this indicates an increase in the hydrophobicity of the surface.

Thus, it turned out that in order to achieve the greatest hydrophobicity of the surface of textile materials, it is necessary to conduct processing in a solution of $AlCl_3$ solution with a concentration of 25–35 g/l. This treatment allows you to achieve a contact angle of wetting of the surface of more than 150⬚.

The contact angle on all samples was also measured again after 30 days and its values did not change. It can be concluded that environmental factors do not harm the coating, and it is durable.

Conclusions

As a result of the study for the production of a hydrophobic surface of textile materials by «wet» chemistry approach, it was found that it is advisable to use a solution of $AlCl_3$ rather than $KAl(SO_4)$ solution. The use of this solution with concentrations of 25–35 g/l allows you to reach a contact angle of wetting of more than 150⬚. As the XPS analysis showed, the hydrophobicity of the surface is ensured by the formation of alumina on the surface of the samples. The character of the dependence of the contact angle on the concentration of the $AlCl_3$ solution was experimentally determined. The wetting angle is directly proportional to the increase in the concentration of $AlCl_3$ solution in the studied range of parameters. When processing coarse calico samples in a solution of aluminum chloride, the hydrophobic coating is durable, even when checking the contact angle after 30 days, it remains. Testing of the coating under physical impact, as well as when washing samples, was not carried out, but similar experiments are planned in further studies.

Declarations

References

Bahners T. et al. Recent approaches to highly hydrophobic textile surfaces, J. of Adhesion Sci. and Technology. 22 (3-4) (2008) 285-309. https://doi.org/10.1163/156856108X295437

Belhaj Khalifa I., Ladhari N. Hydrophobic behavior of cotton fabric activated with air atmospheric-pressure plasma, The J. of The Textile Institute. (2019) 1-7.
 https://doi.org/10.1080/00405000.2019.1688907

Çay A. et al. Application of textile waste derived biochars onto cotton fabric for improved performance and functional properties, J. of Cleaner Production. 251 (2020) 119664. https://doi.org/10.1016/j.jclepro.2019.119664

Cherston J., Paradiso J. A. SpaceSkin: development of aerospace-grade electronic textile for simultaneous protection and high velocity impact characterization, Sensors and Smart Structures Technologies for Civil, Mechanical, and Aerospace Systems. 10970 (2019) 109700J. https://doi.org/10.1117/12.2513962

Daoud W. A., Xin J. H., Tao X. Superhydrophobic Silica Nanocomposite Coating by a Low-Temperature Process, J. of the American ceramic society. 87(9) (2004) 1782-1784. https://doi.org/10.1111/j.1551-2916.2004.01782.x

Gaiolas C. et al. Cold plasma-assisted paper recycling, Industrial Crops and Products. 43 (2013) 114-118. https://doi.org/10.1016/j.indcrop.2012.07.016

Gao L., Thomas J. McCarthy. Wetting and Superhydrophobicity, American Chem. Society. (2009). https://doi.org/10.1021/la903043a

Holme I. Innovative technologies for high performance textiles, Coloration Tech. 123 (2) (2007) 59-73. https://doi.org/10.1111/j.1478-4408.2007.00064.x

Hyde G. K., et al. Atomic layer deposition and abrupt wetting transitions on nonwoven polypropylene and woven cotton fabrics, Langmuir 26 (4) (2010) 2550-2558. https://doi.org/10.1021/la902830d

Karpushko E. N., Bartolomei I. L., Karpushko M. O. Study of using the possibility of textile sand piles at the base of the automobile road folded by saline soils, Procedia Engineering. 150 (2016) 2287-2292. https://doi.org/10.1016/j.proeng.2016.07.298

Liang J. et al. Transformation of hydrophilic cotton fabrics into superhydrophobic surfaces for oil/water separation, J. of the Textile Institute. 104 (3) (2013) 305-311. https://doi.org/10.1080/00405000.2012.721207

Lin D. et al. One-pot fabrication of superhydrophobic and flame-retardant coatings on cotton fabrics via sol-gel reaction, J. of colloid and interface sci. 533 (2019) 198-206. https://doi.org/10.1016/j.jcis.2018.08.060

Marmur A. et al. Contact angles and wettability: towards common and accurate terminology, Surface Innovations. 5 (1) (2017) 3-8. https://doi.org/10.1680/jsuin.17.00002

Molina R. et al. Hydrophobic coatings on cotton obtained by in situ plasma polymerization of a fluorinated monomer in ethanol solutions, ACS applied materials & interfaces. 9 (6) (2017) 5513-5521. https://doi.org/10.1021/acsami.6b15812

Moulder J. Handbook of X-ray photoelectron spectroscopy: a reference book of standard spectra for identification and interpretation of XPS data, Physical Electronics Division, (1992) 261.

Pandit P., Samanta K. K., Teli M. D. Optimization of Atmospheric Plasma Treatment Parameters for Hydrophobic Finishing of Silk Using Box Behnken Design, J. of Natural Fibers. (2020) 1-12. https://doi.org/10.1080/15440478.2020.1745125

Samanta K. K. et al. Hydrophobic functionalization of cellulosic substrates using atmospheric pressure plasma, Cellulose chemistry and technology. 50 (7-8) (2016) 745-754.

Şimşek B., Karaman M. Initiated chemical vapor deposition of poly (hexafluorobutyl acrylate) thin films for superhydrophobic surface modification of nanostructured textile surfaces, J. of Coatings Tech. and Research. 17 (2) (2020) 381-391.

Thierry V., Brown L., Chronopoulos D. Multi-scale wave propagation modelling for two-dimensional periodic textile composites //Composites Part B: Engineering. 150 (2018) 144-156.https://doi.org/10.1016/j.compositesb.2018.05.052

Vohrer U., Müller M., Oehr C. Glow-discharge treatment for the modification of textiles, Surface and Coatings Technology. 98 (1) (1998) 1128-1131. https://doi.org/10.1016/S0257-8972(97)00549-5

Xingfang X et al. Durable superhydrophobic wool fabrics coating with nanoscale Al_2O_3 layer by atomic layer deposition, Appl. Surf. Sci. 349 (2015) 876-879. https://doi.org/10.1016/j.apsusc.2015.05.061

Xu L. et al. Superhydrophobic cotton fabrics prepared by one-step water-based sol–gel coating, J. of the Textile Institute. 103 (3) (2012) 311-319. https://doi.org/10.1080/00405000.2011.569238

Xu L. et al. Fabrication of super-hydrophobic cotton fabric by low-pressure plasma-enhanced chemical vapor deposition, Textile Research J. 89 (10) (2019) 1853-1862. https://doi.org/10.1177/0040517518780000

Xue C. H. et al. Superhydrophobic cotton fabrics prepared by sol–gel coating of TiO2 and surface hydrophobization, Sci. and Technology of Advanced Materials. 9 (3) (2008) 035001. https://doi.org/10.1088/1468-6996/9/3/035001

Xue C. H. et al. Preparation of superhydrophobic surfaces on cotton textiles, Sci. and Tech. of Advanced Materials 9 (3) (2008) 035008. https://doi.org/10.1088/1468-6996/9/3/035008
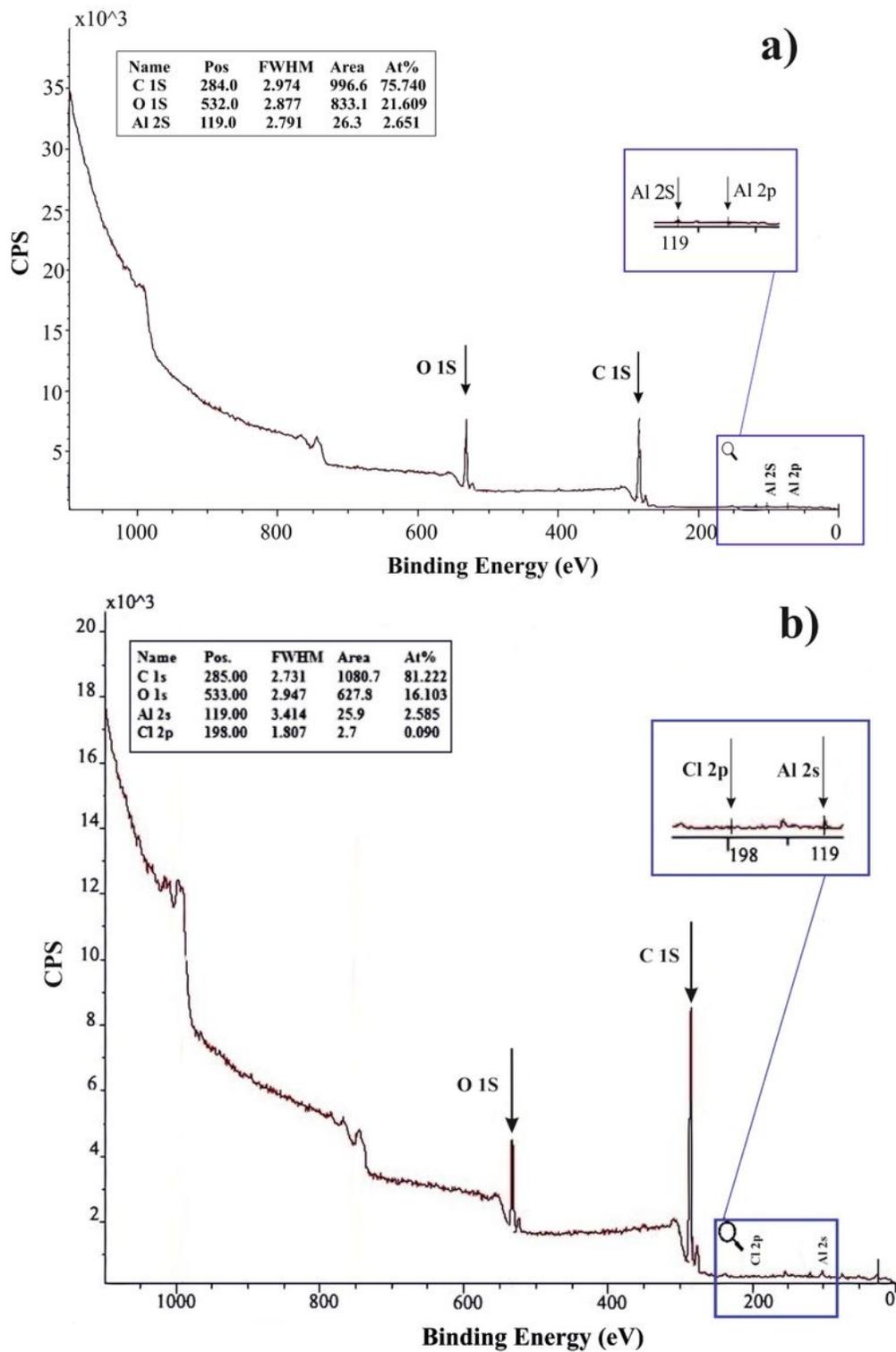
Yang M. et al. Fabrication of superhydrophobic cotton fabric with fluorinated TiO2 sol by a green and one-step sol-gel process, Carbohydrate polymers. 197 (2018) 75-82. https://doi.org/10.1016/j.carbpol.2018.05.075
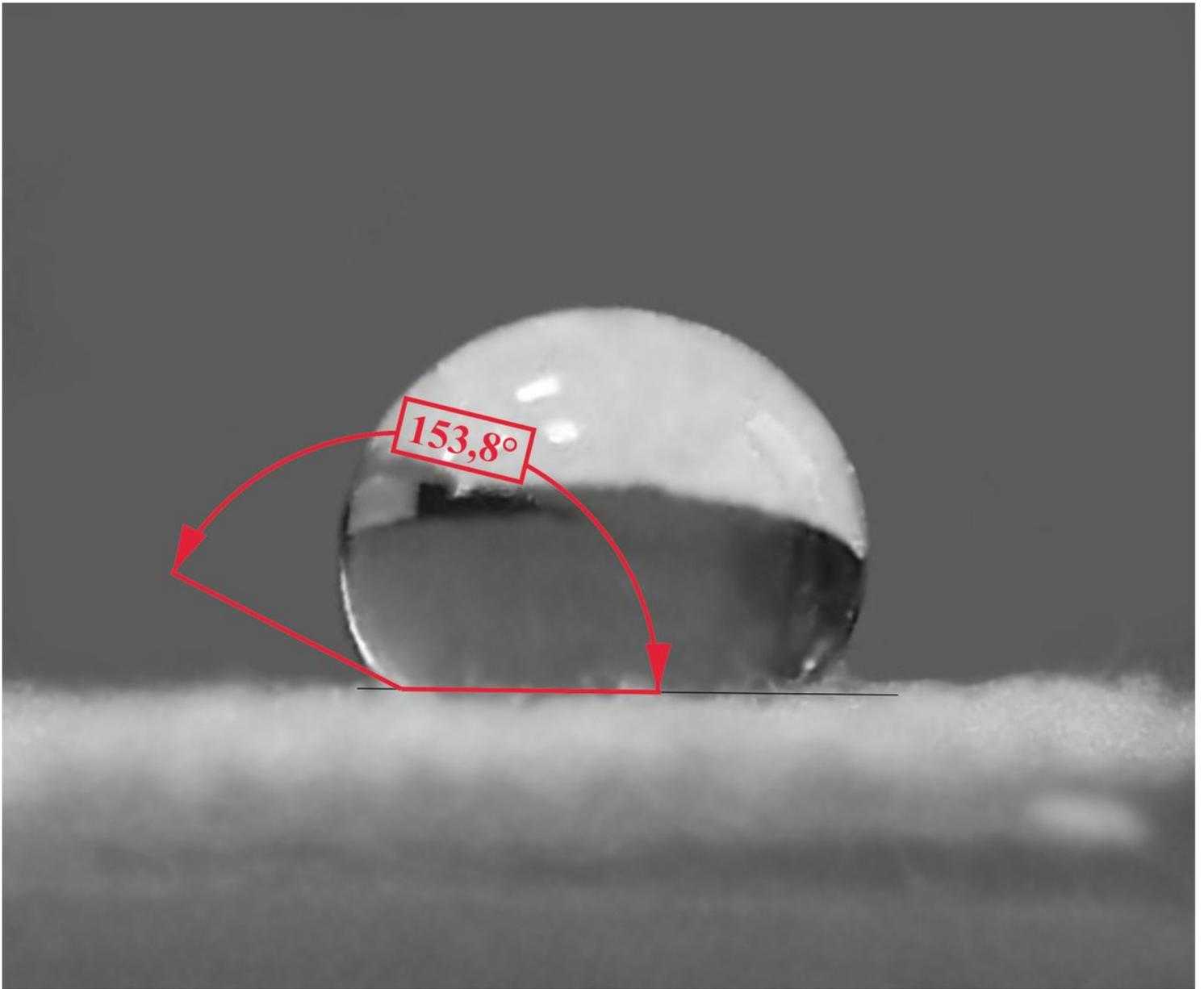
Figures

Figure 1

The contact angle of the sample of textile

Figure 2

(a) – the sample after treatment in solution of KAl (SO4); (b) – the sample after treatment in AlCl3 solution. The results of XPS of coarse calico samples
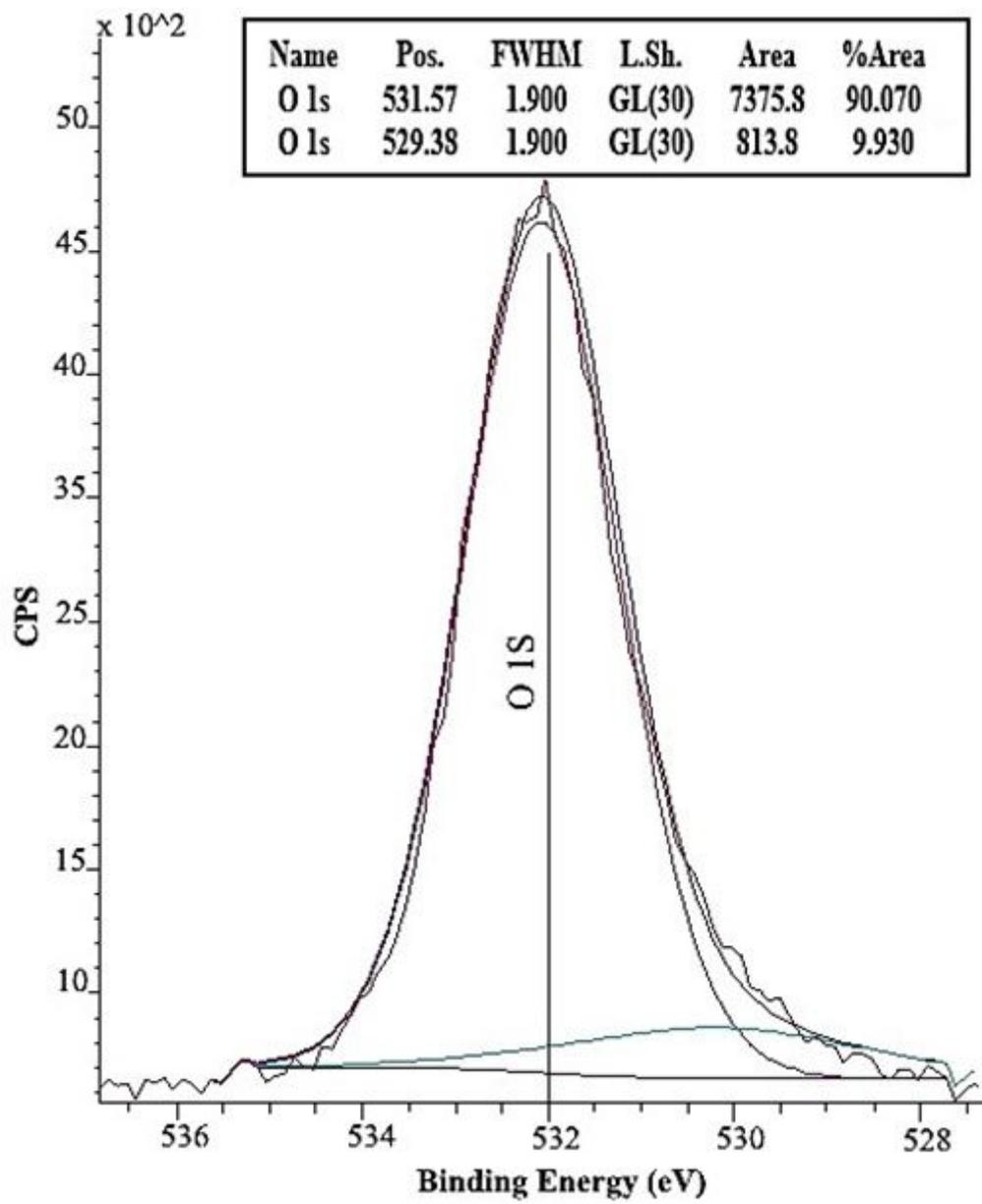
Name	Pos.	FWHM	L.Sh.	Area	%Area
O 1s	531.57	1.900	GL(30)	7375.8	90.070
O 1s	529.38	1.900	GL(30)	813.8	9.930

Figure 3

Oxygen peak decomposition (O1s) of the sample after treatment in AlCl3 solution
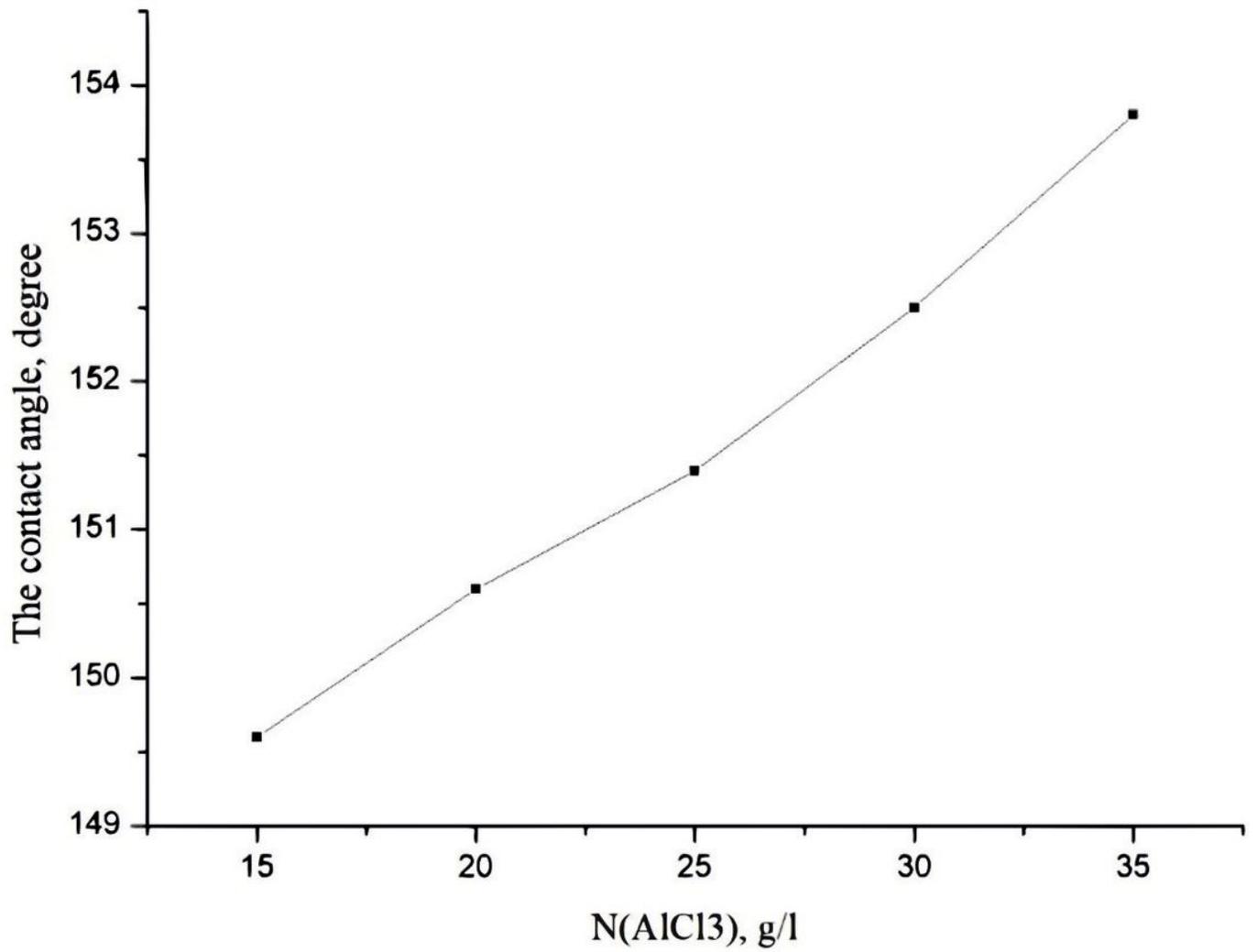
Figure 4

The plot of dependence of the contact angle on the concentration of AlCl3