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Chemo - sorption nonwoven textile materials for purification of waste waters containing Cu^{++}

ABSTRACT

Proposed is a method and product for UV radiation modification of the surface of the needle-felted non-woven metrerial from polyethylene terephthalate standard fibers, for obtaining of ion exchange filters. The fibers obtained should possess a 3D structure and a high hydrolytic stability, which has to guarantee their multiple usage during the numerous sorption processes. As surface modifiers are used Polyethilenimine (PEI), grafted on the surface of the PET fibers with the Epichlorhydrin, Dimethylol dihydroxy cyclic ethylene urea (DMDHEU- $C_5H_{10}N_2O_5$ *, Glyoxal (*$C_2H_2O_2$*). 5.The filter materials obtained are highly effective towards the retention of Cu2+ from industrial waste waters.*

Keywords: *Chemo-sorption, ion exchange filters,water purification.*

1. INTRODUCTION

In order to purify industrial waste waters from hazardous chemical compounds as well as to capture any possible valuable components chemo-sorption agents are usually effectively used.

For this purpose not only granulated but also fibrous materials – most often non-woven textile materials are used. Most suitable of them consist of modified fibers, which surface is capable to enhance substantially ion-exchange, complex-forming, and oxidation - reduction reactions taking place on the surface. This is due to the fact that their relative surface to unit volume or weight of the material is at least twice as big as in the case of granulated materials. This circumstance accelerates the sorption processes and allows much better capture of hazardous and/or valuable compounds. The three possible mechanisms cannot be separated and in most cases act simultaneously, most often sorption and complex formation, sorption and ion-exchange. The various forms of chemo-sorption fibrous materials (fleece of fibers, threads, yarns, textiles, non-woven materials and powders) allows their useful application in apparatuses of different construction and dimensions as well as the realization of continuous process of sorption and desorption. The methods for production of chemo-sorption fibers are most often as follows:implanting polymerization or poly-condensation of active chemo-sorption polymers to an existing fiber; production of fibers of copolymers and/or blended polymers containing groups making possible the chemo-sorption; polymer analogous transformation of macromolecules to fibers [1].

No depending on the method used the fibers obtained should possess a 3D structure and a high hydrolytic stability, which has to guarantee their multiple usage during the numerous sorption processes. Depending on the alkali behavior of the polymer groups two classes of anions exchange fibers – basic and weak basic can be distinguished.

In the presence of acid groups ampholytes of different capacity, depending on the pH of the solution are obtained. It has been established [2] that most of the compounds with basic properties and on the basis of ampholytes are capable to build complexes with Cu^{+}, Cd^{2+}, Cu^{2+}, Fe^{2+}, Zn^{2+} cations (Fig.1).

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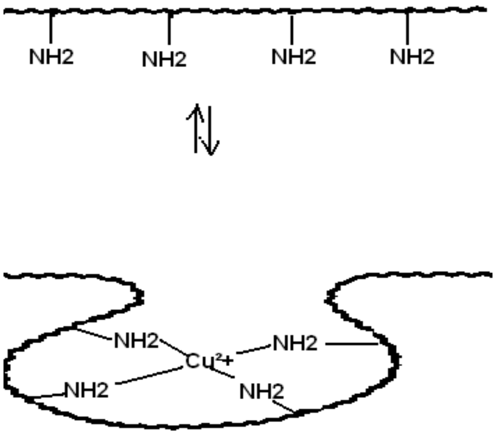


Figure 1 - Schematic presentation of complex formation

In order to modify the surface of PES fiber carriers high molecular polyethilenimin was used. The possibility for the formation of insoluble film with big amount of active amino- and imino- groups was studied. For this purpose dialdehyde or reactant cross-linking agent were used. The last one is similar to this used for impartment of crease-proof to cellulose fibers. It possesses at least four reactive hydroxyl groups. Due to the fact that aliphatic amines react relative quickly with compounds containing aldehyde or hydroxyl groups several questions arise, which should be elucidated:

Consequence of deposition of the products and is it possible to preserve the effect by soaking with preliminary produced cross-linked polymer?

Is it possible to replace the heat treatment of the preliminary soaked fibers with type treatment, low energy source as low temperature plasma by using different kinds of gases, UV radiation, Corona discharge?

What is the influence of the carrier – the fiber type of the fleece (PET, PP, PAN) as well as the technology of fleece production – needle felting, Malivlies?

The influence of pH on the retention, maximum capacity of load and elution assays must be determined.

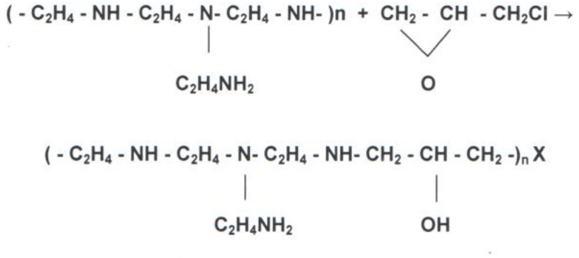
The aim of this study is to elucidate the effectiveness of chemo-sorption filter material on the basis of PES fibers, obtained by two-stage soaking with cross-linking means and polyimine.

2. MATERIALS AND METHODS USED

The following products and materials were used during the course of this study:

Polyethilenimine (PEI) – the trade products on this basis possess a molecular mass of 30 -100 thousand are used in the paper production from wood-containing pulp and recycled paper. Te ca very effective retention and dewatering aid, very effective for increasing the drainage rate in the press section of the paper machine, effective over a wide pH range.

Polyehylenimine is a polymer product of monomers called ethyleneimine. It acts as strong basic and ramified molecule whose aminogroups protonate by addition of water. According to this it is existent in aqueous solution as polycation (Fig.2).



$$(-C_2H_4-NH-C_2H_4-\underset{C_2H_4NH_2}{N}-C_2H_4-NH-)_n + \underbrace{CH_2-CH}_{O}-CH_2Cl \rightarrow$$

$$(-C_2H_4-NH-C_2H_4-\underset{C_2H_4NH_2}{N}-C_2H_4-NH-CH_2-\underset{OH}{CH}-CH_2-)_n X$$

Figure 2 - Schematic presentation of Polyehylenimine

Every third atom of PEI is a protonable amino nitrogen atom, which makes the polymeric network an effective "proton sponge" at virtually any pH.

PEI is a positively charged organic polymer that has gained recent attention as a transfection reagent. A less known use of this cationic polymer as an attachment factor was explored with several cell lines. It is an effective attachment factor for weakly anchoring cell lines and primary cells. Resins with retention properties for copper (II), and uranium (VI) have been synthesized by cross-linking of polyethyleneimine with 1,4-dibromo-2-butene and subsequent alkylation with dimethyl sulphate [3].

The used in this study PEI posses the trade name Polymin SK (BASF, Germany) is 50% solution of polyimine of 30 000 DP molecular weight and is recommended for production of filter paper and impregnation bases. Special features: cleans up white water by fixing anionic substances to the paper, very effective in combination with other cationic and anionic polyacrylamides, lowers the chemical oxygen demand (COD) of the white water.

By the production of film of 3D chemo-reactive polymer instead of Epichlorhydrin, who possesses a high reactivity but is also toxic and carcinogenic substance with sharp obnoxious odour, the following compouds are used: Dimethylol dihydroxy cyclic ethylene urea (DMDHEU- $C_5H_{10}N_2O_5$) and Glyoxal (Etandial-$C_2H_2O_2$).

Dimethylol dihydroxy cyclic ethylene urea (DMDHEU- $C_5H_{10}N_2O_5$) - trade name Fixapret COF from BASF, Germany, with the following structure (Fig. 3):

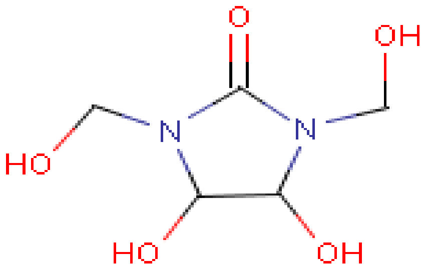


Figure 3 - Schematic presentation of DMDHEU- $C_5H_{10}N_2O_5$

It is a crosslinking agent for durable press finishing of woven and knitted fabrics composed of cellulosic fibres and their blends with synthetic fibres with good reactivity.

Glyoxal ($C_2H_2O_2$) from Fluka Chemie GmbH, Switzerland - it is used in aqueous solution. Glyoxal is existent as Dihydrat HOC-COH.

As a basis needle-felted non-woven material with surface density 400 g/m^2 is used, from PET fibres 3,4dtex, 57 mm. Before the soaking the samples are washed at 60° C with water in ultrasound bath for 2 min in order to replace the auxiliary means or other impurities during the fleece production The drying process is accomplished at 105° C.

The samples were soaked consequently by using a foulard as a first step with Fixapret COF 150 g/l or aqueous solution of Glyoxal 50 g/l, by loading the upper shaft with 40 kg. After that the samples are dried at 80^{o}C. The second step is soaking in a bath of 150 g/l Polyimin SK, followed drying at 80^{o}C. Polycondensation was carried out by two different ways – heat treatment at 130^{o}C for 3 min or 5 min treatment with UV light of 256 nm wavelength.

The mass of the samples in grams was determined before and after the polycondesation and washing. After acclimatization at 20^{o}C and humidity of 62 %, the sample thickness in mm was measured with thickness meter Louis Schopper at 1kPa pressure.

The sample air permeability Bp (l/m^{2}s) was measured with the aid of Texttest FX 3300 from both sides of the sample.

The quantity of retained Cu^{2+} was determined spectrophotometric by using a Xion 500 Dr.Bruno Lange GmbH&Co.KG with LCK 529 cuvets. It happened after soaking the samples into 50 ml 0,0069 g/l aqueous solution of $CuSO_4$ at different temperatures, duration, and pH of the solution. The amount of Cu^{2+} in starting solution was 2,36 and 3,4 mg/ml, respectively. The calculations were carried out by using the difference between the ion content in the starting solution and in the solution at 0^{o}C after a definite period of time. The different types of treatment are presented in Table 1.

Tabel 1 - The different types of treatment

Sample №	Way of treatment
0	As-received sample of needle-felted non-woven textile material
1	Consecutive soaking with Fixapret COF and Polymin SK, T= 130^{o}C
2	Consecutive soaking with Fixapret COF and Polymin SK, T= 130^{o}C, washing
3	Consecutive soaking with Fixapret COF and Polymin SK, T= 130^{o}C, UV 256nm
4	Consecutive soaking with Fixapret COF and Polymin SK, T= 130^{o}C, UV 256 nm, washing
5	Consecutive soaking with Glyoxal and Polymin SK, T= 130^{o}C
6	Consecutive soaking with Glyoxal and Polymin SK, T= 130^{o}C C, washing
7	Consecutive soaking with Glyoxal and Polymin SK, T= 130^{o}C, UV 256nm
8	Consecutive soaking with Glyoxal and Polymin SK, T= 130^{o}C, UV 256nm, washing
9	Simultaneous soaking with Fixapret COF and Polymin SK, T= 130^{o}C
10	Simultaneous soaking with Fixapret COF and Polymin SK, T= 130^{o}C, washing
13	Simultaneous soaking with Glyoxal and Polymin SK, T= 130^{o}C
14	Simultaneous soaking with Glyoxal и Polymin SK, T= 130^{o}C, washing

3. RESULTS AND DISCUSSION

It is well known that Cu^{2+} ions build complexes with 4 molecules ammonium or with two molecules ethylendiamine (see Figure 1). Along with increasing the length of the aliphatic imine chain nitrogen atoms become more alkali which leads to increased effectiveness and better mechanical properties of the deposited onto the surface of the fibers polymer. When proceeding in homogenous medium the reaction rate depends strongly on temperature and the type of the dissolver. The highest reaction rate is observed in aqueous solution in the temperature range 20 – 50°C. However this temperature range is too low when this reaction is used for modification of textile fibers by the soaking method. This is especially the case when working with non-woven textile materials with highly developed surface. The recommended temperature range here is 110 – 150°C. This is why at first study on the influence of temperature and UV 256 nm radiation upon the film obtained by using Fixapret COF and Polymin SK, and Glyoxal and Polymin SK was carried out (Fig 4). This study has shown that the color and the evenness depend strongly on the temperature. After drying at 80°C and heat treatment at temperatures higher than 130°C the color of the film becomes brown, it shrinks and cracks. This is especially strong expressed when working with Glyoxal hydrate. When using 256 nm UV radiation after drying these effects are observed in considerably lower degree.

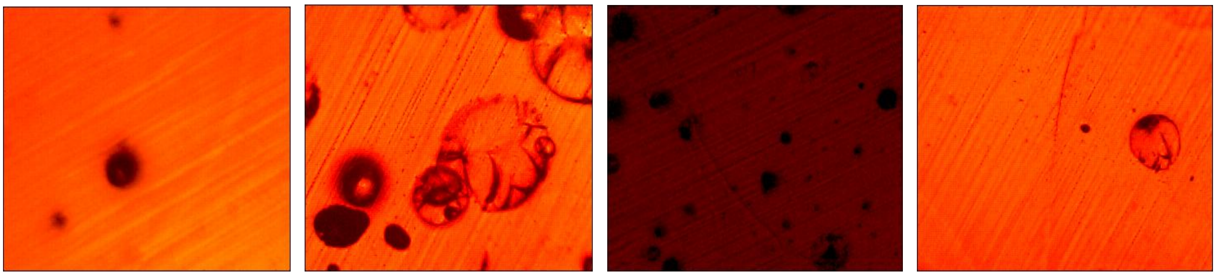


Fig. 4.a *Fig.4.b* *Fig. 4.c* *Fig. 4.d*

Figure 4 - Photos of a film obtained from: 4.a: Glyoxal and Polymin SK, drying at 80°C and heat treatment at 120°C for 3 min. 4.b: Glyoxal and Polymin SK, drying at 80°C and heat treatment for 3 min at 130 °C 4.c: Glyoxal and Polymin SK, drying at 80°C and heat treatment for 3 min at 150°C 4.d Glyoxal and Polymin SK, drying at 80°C and heat treatment with UV 256nm radiation.

The same effect is observed also by working with non-woven textile material. Simultaneously with it changes of sample dimensions is observed, which is evidence for the formation of polymer film on the fiber surface. The amount of the retained product is different bu using Fixapret COF and Polymin (samples 1, 3), and Glyoxal and Polymin SK (samples 5, 7), as well as after heat treatment and treatment with UV 256 nm radiation.

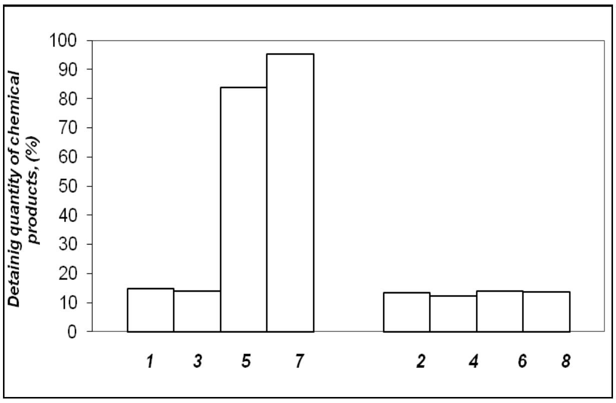


Figure 5 -Amount of retained polymer before and after cleaning of treated samples.

After washing, however, equal amount of active substance upon the sample is retained. This amount is 13.5 % in the case of a film produced from Fixapret COF and Polymin SK and heat treatment. The amount of the same film after UV 256 nm radiation treatment is unsubstantially lower – 12.4 %. After treatment with Glyoxal and Polymin SK followed by heat treatment the amount of retained polymer is 13.6%, while after Treatment with UV 256 nm radiation it is 12.3 % (Fig. 5). As is seen, at the above described soaking conditions the amount of the retained product is equal, and most probably is defined by the amount of free hydroxyl groups which are able to react with the aldehyde and the dimethyilol compound to produce the cross-linked polyimine. The replacement of consecutive soaking with soaking with preliminary blended components does not lead to any change of polymer amount after washing.

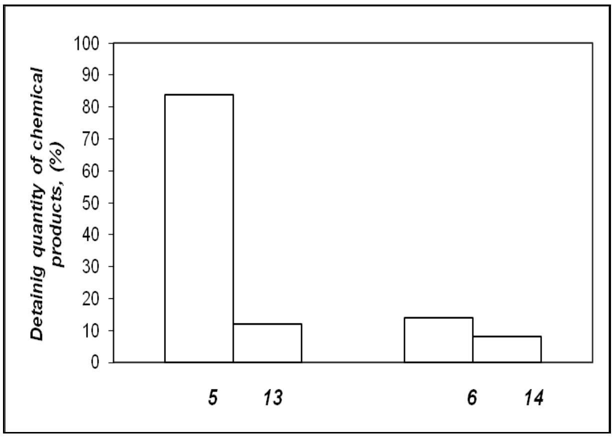


Figure 6 - Comparison of the amounts of polyimine film retained after consecutive and simultaneous with Glyoxal and PISK, followed by heat treatment.

The difference, however, before and after washing is considerably smaller. This is most probably due to the fact that the processes of cross-linking begin already in the soaking bath at room temperature, and a big amount of the polymer is cross-linked and retained in the bath, and cannot be deposited onto the non-woven textile product by using the foulard method. The amount of the retained polymer before and after washing is 11.9 and 8.2 %, respectively (Fig 6). It seems that the consecutive soaking is more effective for increasing the weight gain as compared to the simultaneous soaking. However, additional proof is needed in order to make a final decisive conclusion.

After heat and UV treatment the sample thickness changes and the samples become more stiff. The statistically considered values are given in Table 2.

Table 2 - The statistically considered values

Sample №	Mean sample thickness $\bar{x}$, (mm)	Mean quadratic deviation, s (mm)	Variation coefficient CV (%)
0	3.828	0.069	1.806
2	3.451	0.055	1.605
4	3.485	0.067	1,919
6	3.566	0.071	1,980
8	3.588	0.076	2,108

The thickness of the untreated sample is the biggest, and decreases after different kinds of treatment. As far as the measurements were carried out by using one and the same sample, the influence of the fleece unevenness was omitted (Fig 7). And yet, except sample No. 2, an increase of the variation coefficient CV is observed, which demonstrates a decrease of the thickness evenness of the samples. They become stiffer and visibly change their color, similar to film color – see Figures 4.a -4.d.

The air permeability measurements were statistically evaluated. The measurements were carried out independently for both sites (0, 2, 4, 6, and 8 in the direction of needle punching, and 0', 2', 4', 6, and 8' – in the opposite direction). The both groups of results have shown negligible differences (Fig 8). In both cases a decrease of the air permeability after the polymer film formation is observed. Most probably the polymer films covers not only the fiber surface but also causes the appearance of segmental structure with partial decrease of pores cross section area). This is typical for strengthened non-woven textile materials according the full soacing method. The punching strength increases at least with 15 % [4,5].

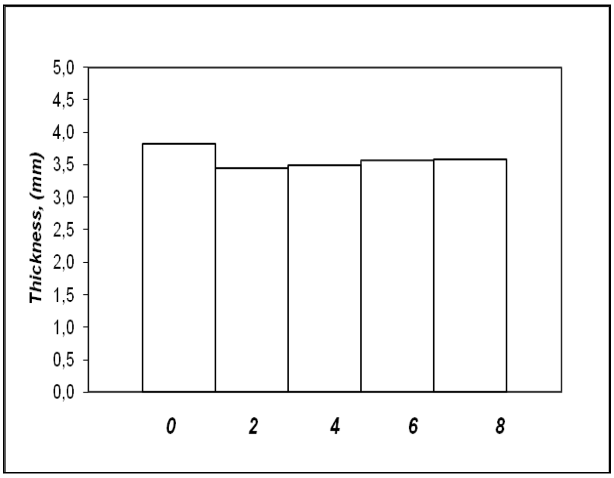


Figure 7 - Comparison of the thickness means values of the filters

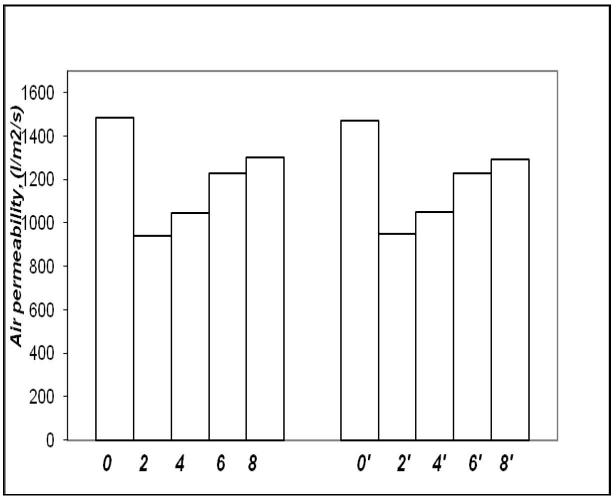


Figure 8 - Comparison between the mean values of filter air permeability.

After soaking of a sample of NWTM for 10 min in 0,069 g/l aqueous solution of $CuSO_4$ at 23^oC a considerable difference in amount of the retained Cu^{2+} ions depending on the type of polymer after-treatment of the modified samples can be established (Fig 9). In spite of the fact that the amount of the deposited polymer after heat treatment is greater as compared to the filters subjected to UV treatment, the last one are more effective by the copper ions retention. Aglomeration of CuSO4 particles on the sample surface is observed. The results from three parallel measurements are shown in Table 3.

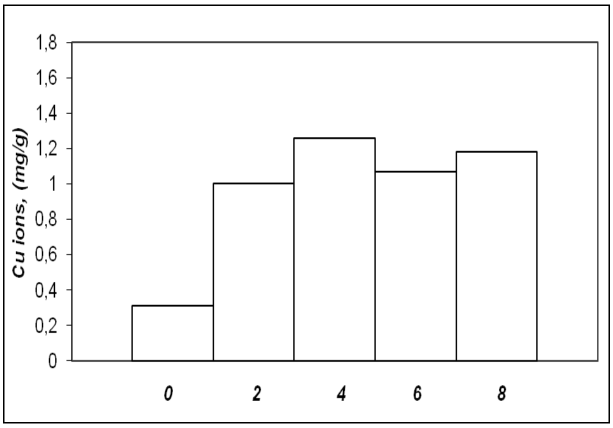


Figure 9 - Retention of Cu^{2+} ions at room temperature

Table 3 - The results measurements aglomeration of CuSO4 particles on the sample surface

Sample №	**Mean sample retention of Cu^{2+} $\bar{x}$ (mg/g)**	**Mean quadratic deviation, s (mg/g)**
0	0,31	0.08
2	1,0	0.14
4	1,26	0.14
6	1,07	0.33
8	1,18	0.05

As far as the results for both types of polymer after-treatments as similar, it could be concluded that most probably the UV poly-condensation treatment causes smaller degree of cross-linking and in this way easier approach of Cu ions to the active centers of the polymer film. Increasing the temperature to 60°C leads to increased Cu ion retain, most probably due to the increased solubility of $CuSO_4$ (Fig 10).

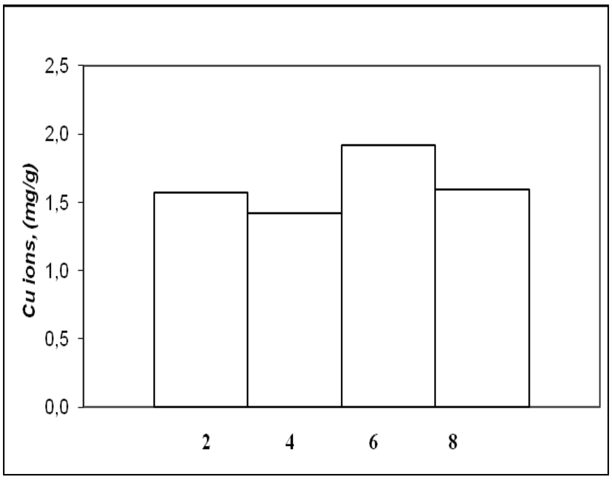


Figure 10 - Cu^{2+} retention at 60°C

Table 4 - The results of measuring efficiency filters

Sample №	**Mean sample retention of Cu^{2+} $\bar{x}$ (mg/g)**	**Mean quadratic deviation, s (mg/g)**
2	1,57	0,32
4	1,42	0,53
6	1,92	0,57
8	1,59	0,80

Although some differences in the results obtained from the three parallel measurements exist this could be explained with the varying to some extent highly developed filter surface of the cassette filters and it is not be expected that effectiveness of the filters will be substantially influenced (Table 4). The increase of $CuSO_4$ concentration in the solution leads to a decrease of the amount of the retained copper ions at preserved soaking time of 10 min. In such cases most probably the soaking time must be increased in order to enhance the diffusion into the filter volume (Fig 11).

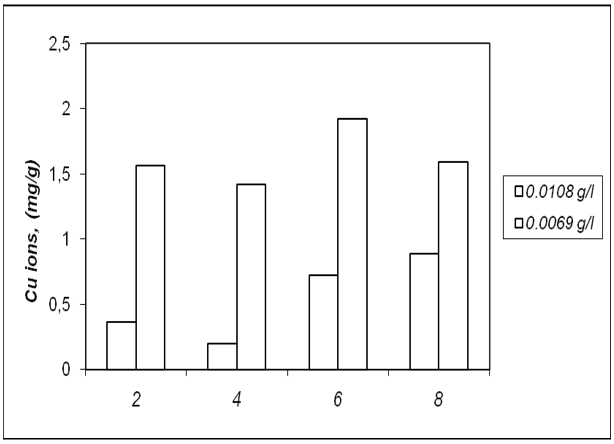


Figure 11 -Cu^{2+} retention at 60°C and different concentrations of $CuSO_4$ solution

While at lower solution concentration the solution discolors after filter soaking, at higher concentrations it still visibly appears green. Increase of the filter soaking time shows that for the four filter materials studied the retained amount of copper ions actively increases till 15 min soaking time and after that retardation of the process takes place till 30 min soaking time. Than saturation of the filters occurs. During this intermediate period between 15 and 30 min soaking time is due to the need of ion diffusion to come into contact with active centers in the volume of the filter (Fig 12).

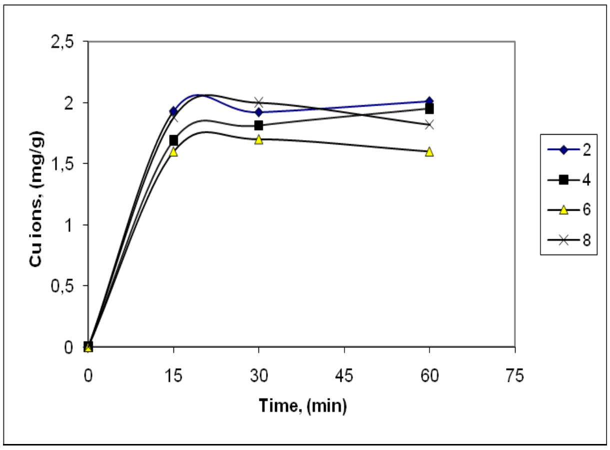


Figure12 - Influence of the soaking time on the degree of copper ion retention at 23^oC and 0.0069 g/l $CuSO_4$ concentration

The samples 6 and 8 show also a beginning of de-sorption after 60 min soaking time. However, times of 60 min for filtration of liquids are unrealistically long. pH of the solution is also of importance. The pH influence is higher by the samples modified with polymer Fixapret COF and Polymin SK. The highest copper ion retention by sample No. 2 is observed at pH 7, and for sample No. 4 the lowest retention is observed at pH 4. Not so substantial are the differences of the samples modified with polymer on the basis of Glyoxal and Polymin SK. In spite of type of the after-treatment – heat treatment or UV radiation, the best retention is obtained at pH 9,5 (Fig 13). The most effective is the treatment of sample No.8 no matter of pH of the solution. It means that the modifying polymer on the surface of PES fibers acts not only as a chemo-sorption medium but also complex former.

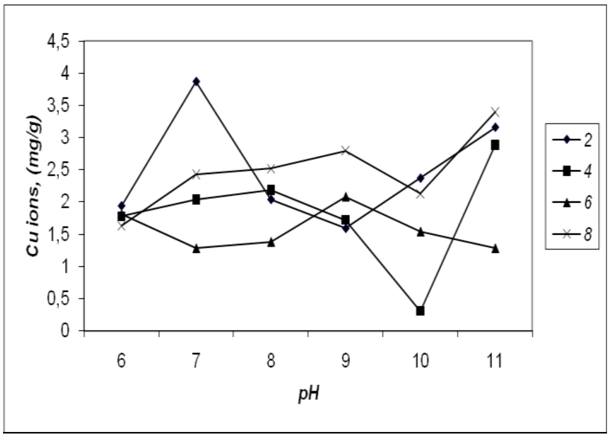


Figure 13 - Influence of pH of the solution on the retention degree at 23^oC and 0.0069 g/l concentration of the $CuSO_4$ solution.

The degree of $CuSO_4$ retention on the filters of NWTM at room temperature and 10 min soaking time is illustrated also by the photos shown in Fig. 14 – see also Table 5.

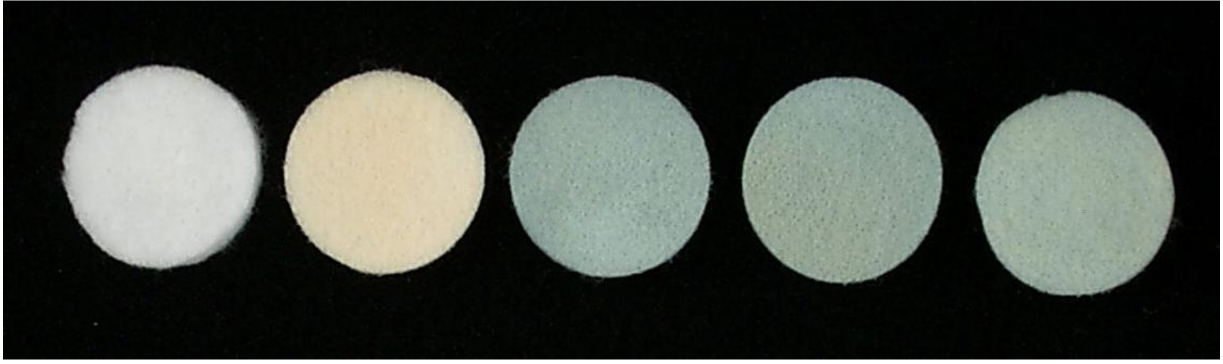


Figure 14 - Comparison between samples before and after retention of $CuSO_4$.

Table 5 - The degree of $CuSO_4$ retention on the filters of NWTM

Filter type	**Retention of Cu^{2+} (%) At 0,0108g/l solution concentration**	**Retention of Cu^{2+}(%) at 0,0069 g/l solution concentration**
2	5.39	35.70
4	2.99	32.31
6	10.78	43.65
8	13.17	35.80

In order to estimate the treatment effectiveness additional study on another sequence product application and on the possibility to use one stage soaking have to be carried out. It was established that by the application firstly of the low molecular compound Fixapret COF or Glyoxal, after that Polymin SK the weight gain is 12 – 13 %, leading to 32 – 44 % purification. The results obtained from samples treated with Glyoxal are better.

4. CONCLUSIONS

1. Chemo-sorption polyester fibers were obtained via deposition of a surface polymer film.with great number of active sorption sites of amine and imine nature.
2. The results obtained from samples treated with UV radiation are better concerning the effectiveness filter medium as compared to the results from samples subjected to heat treatment.
3. The Polymer obtained via condensation of Glyoxal and PISK, especially after UV radiation treatment, is more effective, although the weight gain is lower.
4. Additional study on the influence of reverse sequence of compound application, as well as the possibility simultaneous application has to carried out.
5. The filter materials obtained are highly effective towards the retention of Cu^{2+} from industrial waste waters.

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IZVOD

HEMOSORPCIJA NETKANIH TEKSTILNIH MATERIJALA ZA PREČIŠĆAVANJE OTPADNIH VODA KOJE SADRŽE Cu^{2+} JONE

Predložena je metoda i proizvod od UV zračenja modifikovanih površina netkanog metreriala od polietilen-tereftalat standardnih vlakana, za dobijanje jonoizmenjivačkih filtera. Dobijena vlakna treba da poseduju 3D strukturu i visoku hidrolitičku stabilnost, koja mora da garantuje njihovu višestruku primenu tokom brojnih sorpcionih procesa. Kako se koriste površinski modifikatori polietilenimina (PEI), kalemljeni na površini PET vlakana sa epihloridinom, dimethiloldihidroksi ciklični etilen urea (DMDHEU- $C_5 H_{10}N_2O_5$, glioksalni ($C_2H_2O_2$)$_5$. Dobijeni filterski materijali su visoko efikasni za zadržavanje Cu^{2+} iz industrijskih otpadnih voda.

Ključne reči: *Hemosorpcija, jonoizmenjivački filteri , prečišćavanje vode.*

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