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MODIFICATION OF CHEMICAL FIBERS WITH PLANT POLYPHENOLS TO IMPROVE THEIR SORPTION PROPERTIES

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The purpose of the research is to create new combined composite fibrous materials for the sorption of heavy metal ions from waste water of industrial enterprises. To study the sorption capacity of the sorbent, the content of Fe^{3+} in model solutions was determined by analytical methods before and after sorption, the maximum recovery ratio for Fe^{3+} was calculated, %; chemical fibers were studied before and after treatment with tara/quebracho tannins and iron (III) compounds to determine the mechanism of interaction with plant polyphenols by the FTIR spectroscopy. It was established that interaction of Fe^{3+} with chemical fibers treated by polyphenols probably occurs as a result of the formation of coordination bonds between neighboring hydroxyl groups of the aromatic ring one molecule and the C=O group of the unsaturated aromatic ring of another polyphenolic molecule or due to the formation of chemical bonds with CO groups of modified chemical fibers. Sorption of Fe^{3+} ions after treatment of the fibrous sorbent with tara tannins at a temperature of 40 °C is higher than after treatment with quebracho tannins under similar conditions. Treatment during the first four hours is most effective. At the same time, the maximum recovery ratio for Fe^{3+} reaches 90%. The advantages of the obtained sorbent include high sorption activity and the ability for further modification, the methods of preparation are quite simple and cheap, and the possibility of producing the sorbent from secondary raw materials helps to solve the problem of utilization of fibrous waste.

Keywords: sorption properties, chemical fibers, plant polyphenols

INTRODUCTION

Waste water from textile or leather industry enterprises, electroplating shops is mostly contaminated with salts of copper, chromium, iron, nickel and other metals. The sorption extraction of metals from wastewater has become quite widespread due to its high efficiency and the absence of secondary pollution. The group of synthetic polymer sorbents includes polypropylene, polyethylene, polyacrylamide (Manju *et al*., 2002), polystyrene, and polyurethane, which are used to manufacture special sleeves, mats, and pillows for sorption of hazardous liquids. Polymer adsorbents have hydrophobic properties, low volume density; sorption capacity can exceed 100 g/g (Li *et al*., 2012; Matveeva *et al*., 2012). Due to their low density and hydrophobicity, they are mainly used in water environments. Mineral adsorbents have such advantages as non-flammability, chemical inertness, relatively low cost and availability. Most mineral adsorbents are used in the form of powder or granules. Mineral sorbents are effective in eliminating oil spills (Bandura *et al*., 2017). Organic adsorbents include peat, moss, dry leaves, straw, sawdust, bark and waste from the processing of cellulosic raw materials (Yu *et al*., 2001; Palma *et al*., 2003; Wahi *et al*., 2013; Hoang *et al*., 2018). Natural organic sorbents are inexpensive, available, environmentally friendly, but their low bulk density limits their use in the aquatic environment.

Fibrous sorption-active materials are increasingly used due to their characteristics, in particular, compared to granular sorbents, they have higher chemical and thermal stability, a homogeneous porous structure and a large active surface area, a significant volume of

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micropores and a high mass transfer coefficient, and installations, in which fibrous materials are used, occupy a much smaller area (Adam *et al*., 2019). In addition, the possibility of production of fibrous sorbents from secondary raw materials allows solving the problem of utilization of leather, textile and polymer production waste.

The authors of the article developed a method of obtaining an environmentally safe polymer composite material with sorption properties from fibrous waste of the textile industry based on high-volume combined loop threads consisting of two components (Fig. 1a). Fibrous textile wastes containing 70% polyurethane fibers 162C (linear density 4.4 tex) and 30% polyamide fibers 6.6 f20/1 (linear density 3.3 tex) were used to obtain a polymeric composite material with sorption properties (Tarasenko *et al*., 2019). Polyurethane fibers are similar in their chemical properties to polyamides, as they equally contain amide groups –NH–CO–, which participate in the formation of hydrogen bonds. However, the additional oxygen atom included in the polyurethane chain –NH–CO–O– gives it greater flexibility, so polyurethanes have a lower melting point compared to polyamides of a similar structure (~178 °C for polyurethane versus 255 °C for polyamide 6.6).

Bicomponent adhesive fibers (BAF) Acebon 4/51 black, 0.44 tex (20 mass. %) were added to the original composition. Acebon 4/51 black are adhesive fibers of the “core-sheath” type, which consist of polyethylene terephthalate (core, T melting point = 265°C) and PET copolymer (the upper low-melting component T melting point = 110°C). Fig. 1b shows a microphotograph of the surface of the non-woven material in reflected light after the thermobonding process. It is noticeable that the heat treatment of the non-woven fabric leads to the melting of the surface layer of bicomponent fibers. At the same time, cohesive bonds are formed at the intersections of such fibers, marked by red arrows on the photomicrograph. At the same time, it is clearly visible that in the places of contact of bicomponent fibers with the main fibrous material (PU/PA-6,6), the formation of adhesive bonds between them takes place (indicated in the photomicrograph by green arrows).

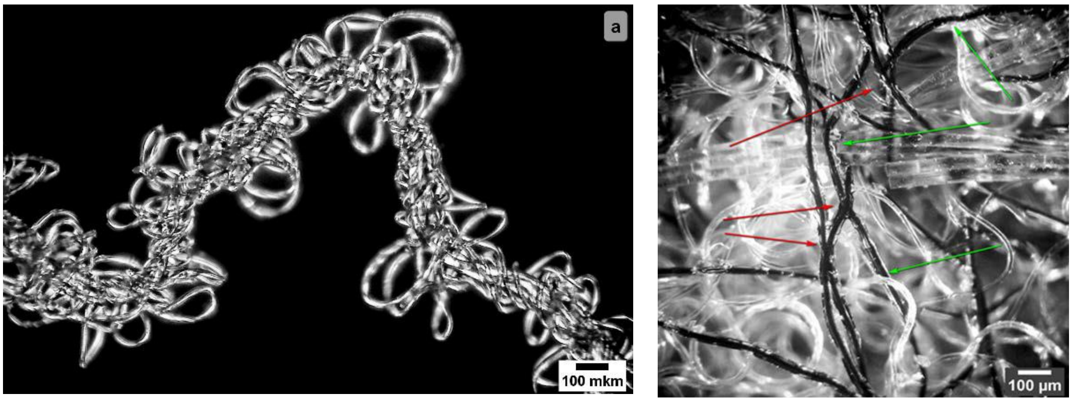

Figure 1. Microphotographs of the fibrous textile wastes: a) high-volume combined loop threads consisting of two components; b) the surface of the non-woven material in reflected light after the thermobonding process

It is of interest to determine an effective method of modifying the natural and synthetic fibers to increase the activity of their functional groups, in particular by the method of controlled chemical destruction, taking into account that the effectiveness of the sorbent depends on the presence of active functional groups that are capable of irreversibly binding heavy metal ions. Chemical destruction of both polyurethanes and polyamides can occur, in particular, under the influence of organic solvents alcohols, acids, alkalis, phenols and their derivatives, and is accompanied by the cleavage of C-N bonds (Nelson, 1976). As a result of this rupture, two macromolecules containing an amino group and a carboxyl group are formed (Fig. 2).

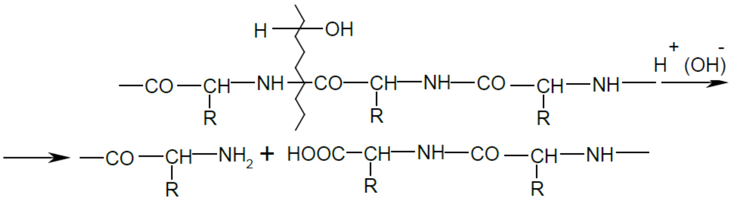

Figure 2. Chemical destruction of both polyurethanes and polyamides

The purpose of the research is to obtain new ecologically safe combined composite fibrous materials based on polyurethane-polyamide chemical fiber waste and to study their sorption properties for water purification from Fe^{3+} ions.

EXPERIMENTAL SECTION

To increase the sorption capacity of fibrous sorbents to iron compounds, the initial fibers were pre-treated with extracts of quebracho (KB) and tara (Tara) tannins, which belong to different classes and differ in the nature of the functional groups of polyphenols in the structure of tannins (Faber, 1990). Tara tannins are obtained from pods of small trees of *Caesalpinia spinosa* or *Caesalpinia tinctoria* species (Bertnet, 2001). Tara tannins belong to the group of pyrogallols, that is, they are hydrolyzed with the formation of a mixture of gallic and ellagic acids (Fig. 3) and have carboxyl and hydroxyl groups in the structure of polyphenols (Vitolo *et al.*, 2003).

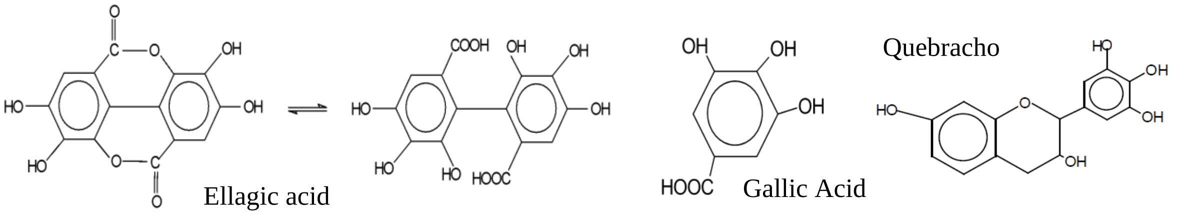

Figure 3. Polyphenols of quebracho and tara tanids

Quebracho is the general name of various tree species (*Quebrachia lorentzii syn. Schinopsis balansae*) of the families *Anacaroliacea* and *Apocunacea*. Quebracho tannins belong to the pyrocatechin group. Quebracho tannins have only hydroxyl groups (Fig. 3) in the structure of polyphenols (Covington and Shi, 1998), and therefore the process of sorption of heavy metals will occur differently.

Pretreatment of Fibrous Sorbents with Plant Extracts

Quebracho and Tara tannins solutions with a concentration of 10 g/l of tannins were used for fiber pretreatment. To prepare a solution of quebracho tannins, a portion of dry extract of quebracho was weighed on an analytical balance (it was taken into account that the content of tannins in the dry extract is 68%), placed in a heat-resistant round-bottomed flask with a volume of 500 ml, 200-250 ml of warm water was added there, the solution was adjusted to boiling to completely dissolve the quebracho extract, then the solution was cooled and quantitatively transferred to a 1000 ml volumetric flask and made up to the mark with distilled water. Similarly, a solution of tara tannins was prepared (the content of tara tannins in the dry extract was 38%).

Fibers were pre-treated for 4 hours at a temperature of 40 °C. The volume of the tannin solution for treating the fibrous sorbent was 10 times greater than the mass of the fibrous material. At the end of the treatment, the tannin-filled fibrous material was wrung out, dried, and later used to determine its sorption efficiency to Fe^{3+} ions (Table 1). A solution of ferric ammonium alum $NH_4Fe(SO_4)_2 \cdot 10H_2O$ with a concentration of Fe^{3+} ions ~10 g/l was used as a model of Fe-containing wastewater. Treatment was carried out at temperatures of 20 and 40 °C, the concentration of Fe compounds in the spent solution was determined after 1, 2, 4 and 24 hours of treatment (Table 1) by the titrimetric method in the presence of sulfosalicylic acid (State Standard of Ukraine 7262:2012). The maximum recovery ratio (RR_{max}) for Fe^{3+} was calculated according to the formula:

$$RR_{max} = \frac{C_{Fe^{3+}initial} - C_{Fe^{3+}finish}}{C_{Fe^{3+}initial}} \cdot 100\% \qquad (1)$$

Table 1. Parameters of treatment of fibrous material with Fe^{3+} compounds

Duration of the fibrous material treatment in Fe^{3+} solution (h) after treatment with tannins	t, °C	A type of tannins for pre-treatment of fibrous material	Content of Fe^{3+} in the initial/spent solution, g/l	The maximum recovery ratio for Fe^{3+}, %
0	20	–	9,97	–
0,5	20	Quebracho	3,89	61,0
1,0	20	Quebracho	3,72	62,7
2,0	20	Quebracho	3,85	61,5
4,0	20	Quebracho	3,80	61,9
24,0	20	Quebracho	3,53	64,6
0	40	–	9,99	–
0,5	40	Quebracho	4,89	51,0
1,0	40	Quebracho	4,76	52,4
2,0	40	Quebracho	3,21	67,8
24,0	40	Quebracho	3,14	68,5
0	40	–	9,97	–
0,5	20	Tara	3,95	60,4
1,0	20	Tara	3,64	63,6
2,0	20	Tara	1,93	80,6
4,0	20	Tara	1,53	84,6
24,0	20	Tara	2,53	75,6
0	40	–	9,91	–
0,5	40	Tara	1,14	88,5
1,0	40	Tara	1,08	89,1
2,0	40	Tara	1,06	89,3
4,0	40	Tara	0,96	90,3
24,0	40	Tara	1,14	88,5

It was determined that the sorption of Fe^{3+} ions after treatment of the fibrous sorbent with tara tannins at a temperature of 40 °C is higher than after treatment with quebracho tannins under similar conditions (Table 1). Treatment during the first four hours is most effective. Then the treatment efficiency decreases significantly, and after a day the reverse desorption process begins.

The interaction features of Fe^{3+} compounds with fibrous sorbent were determined by the method of IR spectroscopy. IR spectroscopic studies were performed on a universal Fourier–IR spectrometer TENSOR-37 (BRUKER, Germany). The test samples were thoroughly crushed and pressed into tablets with KBr. IR absorption spectra were studied in the frequency range of 400...3800 cm^{-1}. The infrared spectra of the studied samples were characterized using the following indicators: A – Gaussian peak area, relative units (r.u.); W – peak half-width, r.u.; ν –

wave number, cm^{-1} (maximum peak). IR spectra were interpreted using tables of characteristic frequencies. The results of IR spectroscopic studies are shown in Tables 2-3, Fig. 4.

Noticeable peaks at 3430, 2920, 2850 and 1640 cm^{-1} observed for all fiber samples are considered by the authors (Huang *et al*., 2019) to be characteristic absorption peaks for polyamide PA 6 (Tables 2-3). The authors (Liang *et al*., 2020) explain the strong absorption peak with a maximum at 3430 cm^{-1} by valence asymmetric vibrations of the N-H group of amides. A strong absorption peak at 1640 cm^{-1} is associated with bending vibrations of amide and water (Yu *et al*., 2019). Symmetrical and asymmetric stretching of -NH$_2$ in both bands shifted to a low-frequency region from the position of the free amino group (3500 and 3400 cm^{-1}), which makes it possible to conclude that the -NH$_2$ groups are involved in the formation of a hydrogen bonds due to the influence of OH groups of polyphenols.

Table 2. Results of IR spectroscopic studies of the fibrous materials samples treated with quebracho polyphenols

Functional groups	Samples								
	PU-PA			PU-PA+KB			PU-PA +KB+Fe		
	A, r.u.	ν, cm^{-1}	W, r.u.	A, r.u.	ν, cm^{-1}	W, r.u.	A, r.u.	ν, cm^{-1}	W, r.u.
δN—H (Longitudinal direction, wagging and twisting vibrations at R-NH$_2$ Ar-NH$_2$)	141	687	190	24	697	66	3	683	23
ν C–O	16	1072	59	30	1062	75	1	1073	14
δ_{as} N—H (Latitudinal direction, scissoring vibrations at R-NH$_2$ Ar-NH$_2$) amide II	119	1544	103	114	1532	90	111	1531	86
ν_s C=O (amide I)	14	1739	56	120	1675	133	133	1670	135
ν_s N–H (R-NH$_2$)	69	3056	121	42	3069	87	54	3069	97
ν_{as} N–H (R-NH$_2$)	344	3307	274	230	3303	220	236	3301	214

Table 3. Results of FTIR spectroscopic studies of the fibrous materials samples treated with tara polyphenols

Functional groups	Samples								
	PU-PA			PU-PA+tara			PU-PA +tara+Fe		
	A, r.u.	ν, cm^{-1}	W, r.u.	A, r.u.	ν, cm^{-1}	W, r.u.	A, r.u.	ν, cm^{-1}	W, r.u.
δN—H (Longitudinal direction, wagging and twisting vibrations at R-NH$_2$ Ar-NH$_2$)	141	687	190	66	704	92	35	700	74
ν C–O	16	1072	59	50	1058	97	28	1055	76
δ_{as} N—H (Latitudinal direction, scissoring vibrations at R-NH$_2$ Ar-NH$_2$) amide II	119	1544	103	132	1539	87	121	1533	93
ν_s C=O (amide I)	14	1739	56	33	1733	67	88	1675	132
ν_s N–H (R-NH$_2$)	69	3056	121	53	3067	96	55	3069	99
ν_{as} N–H (R-NH$_2$)	344	3307	274	253	3302	220	219	3298	199

In the FTIR spectra of polymeric materials treated with quebracho and tara polyphenols and Fe(III) compounds, a change in the shape, height, and half-width of a rather broad absorption band in the region of 3200-3600 cm^{-1} is observed. In this interval, there is an overlap of absorption bands with a frequency of 3300-3500 cm^{-1}, which correspond to N–H bonds of amino groups; 3200-3400 cm^{-1}, which correspond to intra- and intermolecular hydrogen bonds of phenolic compounds and the absorption band of the bound OH group in the region of 3200-3300 cm^{-1}. This confirms the interaction of polyphenols with polyamide-polyurethane fibers and Fe(III) compounds due to hydrogen bonds with the participation of phenolic hydroxyl groups and amino groups of polymeric materials.

Attention is drawn to changes in the low-frequency region of the spectrum (Tables 2-3). The area of the peak, which belongs to δ(N-H) with a maximum of 687 cm^{-1} gradually decreases: 141 r.u. for starting polymer material, 66 r.u. after processing the polymer material with tara polyphenols, 35 r.u. after treatment with Fe^{+3} compounds. This is accompanied by a decrease in the half-width of the peak from 190 to 92 and 74 r.u., respectively. A similar situation is observed after processing the polymer fiber with Quebracho tannins. 190, 66, 23 r.u. – the half-width decreases; 141, 24, 3 r.u. – the area of the Gaussian peak decreases.

There is a shift of the frequency corresponding to νs C=O vibrations to the low-frequency region (1739, 1675, 1670 cm^{-1} after processing the polymer material with quebracho polyphenols and 1739, 1733, 1675 cm^{-1} after processing the polymer material with tara polyphenols). The shift of the absorption peak of the C=O carbonyl group to the low-frequency region indicates the presence of aromatic elements in the system. This is accompanied by increase in the half-width of the band (56 r.u. for starting polymer material, 67 r.u. after processing the polymer material with tara polyphenols, 132 r.u. after treatment with Fe(III) compounds; 133 r.u. after processing the polymer material with quebracho polyphenols, 135 r.u. after treatment with Fe^{+3} compounds).

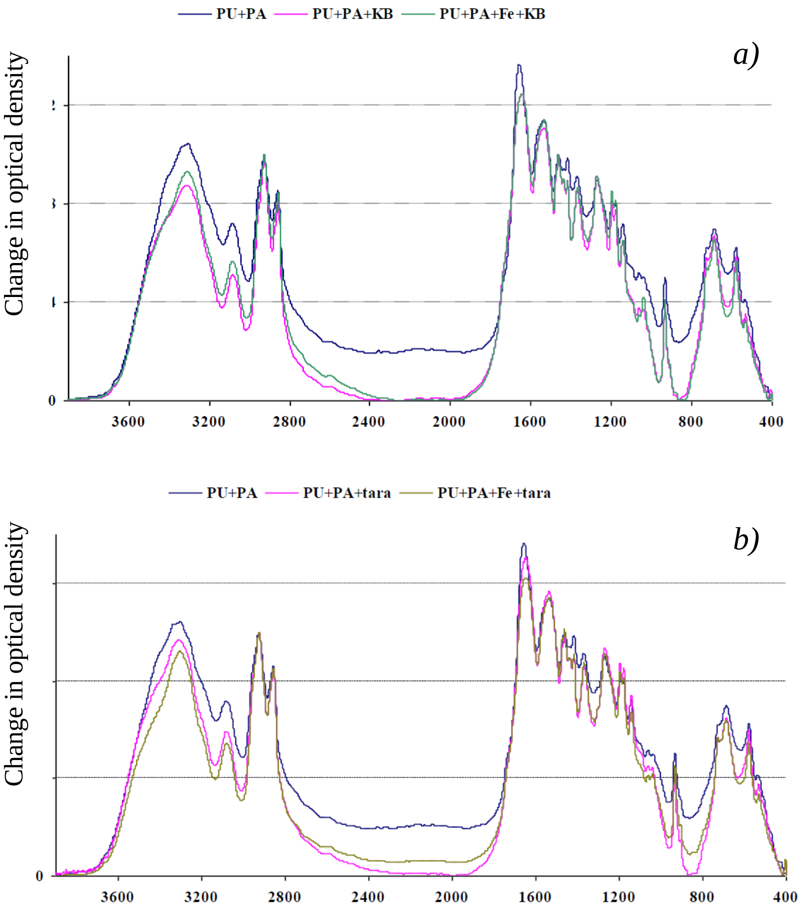

Figure 4. Results of FTIR spectroscopic studies of fibrous sorbent treated by Fe^{3+} and polyphenols Quebracho (a) / Tara (b)

According to the authors (Walenkcik *et al.*, 2024), metal–polyphenols networks are usually formed using coordination bonds during complexation. At the same time, coordination bonds between metal ions and polyphenol molecules are formed with the participation of neighboring hydroxyl groups of the aromatic ring one molecule and the C=O group of the unsaturated aromatic ring of another molecule (Fig. 5). This assumption is fully confirmed by the results of our research. In particular, a similar type of interaction is evidenced by the shift of the absorption band of valence vibrations of C–O bonds ~ 1100 cm^{-1} to the low-frequency region (1052....1073 cm^{-1}), a decrease in the area of the peaks and their half-width as a result of the interaction with metal ions.

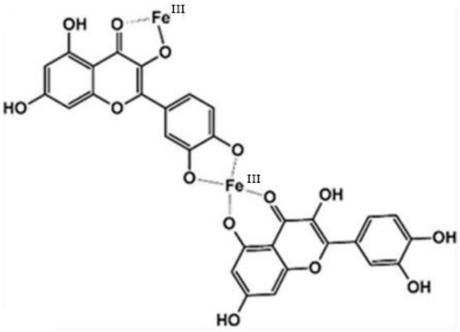

Figure 5. Schematic representation of the coordination interaction of Fe^{3+} ions and plant polyphenol molecules according to Walenkcik *et al*., 2024

That is, the interaction of Fe^{3+} with polyamide and polyurethane fibers treated by polyphenols probably occurs as a result of the formation of coordination bonds between neighboring hydroxyl groups of the aromatic ring one molecule and the C=O group of the unsaturated aromatic ring of another polyphenolic molecule. Perhaps the interaction of Fe^{3+} with the sorbent probably occurs as a result of the formation of chemical bonds with –CO groups of modified polyamide and polyurethane fibers. Prior blocking of amino groups of modified polyamide fibers can contribute to increasing the efficiency of such interaction, in particular as a result of binding with polyphenols and their derivatives, which are usually contained in the wastewater of industrial enterprises. In this way, the problem of complex wastewater treatment may be solved.

CONCLUSIONS

The developed method of the fibrous materials modification is based on the material treatment with tannin solutions of the different chemical structure, the main component of which are plant polyphenols. It was established that the sorption capacity of the fibrous sorbent for Fe^{3+} ions after treatment with tara tannins at a temperature of 40 °C is higher than after treatment with quebracho tannins under similar conditions. Treatment within the first four hours is most effective. At the same time, the maximum extraction rate of iron-ammonium alum solution reaches 90%. It was established by FTIR spectroscopy that the interaction of Fe^{3+} with polyamide and polyurethane fibers treated by polyphenols probably occurs as a result of the formation of coordination bonds between neighboring hydroxyl groups of the aromatic ring one molecule and the C=O group of the unsaturated aromatic ring of another polyphenolic molecule or due to the formation of chemical bonds with CO groups of modified polyamide and polyurethane fibers. Thus, the fibrous waste of the textile industry can be used to obtain an environmentally safe polymer composite material for the purification of wastewater from heavy metal ions. The advantages of the obtained sorbent include high sorption activity and the possibility of further modification, and the production methods are quite simple and cheap.

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