RIGA TECHNICAL UNIVERSITY
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THE DEVELOPMENT OF TREATMENT METHOD FOR PLYWOOD INDUSTRY WASTEWATER, CHARACTERISTIC AND POSSIBLE APPLICATION OF THE OBTAINED COAGULATES

Summary of Ph.D. thesis

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CONFIRMATION

Hereby I confirm that I have worked out the present Doctoral thesis, which I submitted for consideration at the Riga Technical University for acquisition of a Doctoral degree in engineering. The present Doctoral thesis is not submitted in other scientific institutions for acquisition of a scientific degree.

Julija Brovkina …………………………….

Date: 29.11.2012.

The Doctoral thesis is written in Latvian; it contains Introduction, References review (6 chapters), Experimental (7 chapters), Results and discussion (7 chapters), Conclusions, the used References list, 51 Figures, 27 Tables, 1 Appendix and 27 Formulae - a total of 159 pages. The References list has 323 titles.

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Julija B.

TABLE OF CONTENTS

LIST OF SYMBOLS

BOD_5	Biological oxygen demand
^{13}C-NMR	Carbon Nuclear Magnetic Resonance Spectroscopy
DTA	Differential Thermal Analysis
ESI-MS	Electrospray Ionization Mass Spectrometry
FT-IR	Fourier Transform – Infrared spectroscopy
FE-SEM	Field Emission Scanning Electron Microscopy
HLES	Hemicelluloses and lignin substances
KSPAC	Composite coagulants on polyaluminium chloride and aluminium sulphate base
KHPAC	New composite coagulants on polyaluminium chloride base
COD	Chemical oxygen demand
LSV	Lignin containing substances and aromatic substances
LTM	Latvian triassic clay
LTM 011	LTM with modifier based on coagulates (0.11% content)
LTM 011-800	LTM 011 after thermal treatment at 800 ˚C
MW	Model wastewater
NW	Wastewater from hydrothermal basin
PAC	Polyaluminium chloride
PI	Permanganate index
TOC	Total organic carbon

GENERAL DESCRIPTION

One of the most advanced wood processing industries in Latvia is a plywood manufacturing [1]. It should be noted that the integrated enterprises of forestry take a leader position amongst the production sectors by bringing the negative impact on the surrounding environment. Wood processing results in a large amount of wastewater that is characterized by a specific coloration and high chemical oxygen demand (COD).

Topic's actuality is determined by the fact that the European Union has seriously changed requirements of water quality (COD, BOD, suspended solids, colour) for its discharge in the drainage networks [2, 3]. The integrated forestry enterprises, especially plywood industry, is a captive in a situation, in which regulations do not permit the wastewater discharge into the joint drainage system, that does not comply with the maximum permissible requirements of pollution concentration (MPC). In the majority of cases, these plants do not have a centralized wastewater treatment plant [4]. Consequently, there is a problem associated with wastewater treatment technology's replacement or improvement with a view to perfect hemicellulose and lignin containing substances (HLES) removal from a technological flow and re-use purified water for manufacturing needs.

Goal of research

1) to examine the pollutants of wood's origin by means of wood mild hydrolysis using aluminium-containing coagulants and composition coagulants on polyaluminium chloride bases;

2) to examine potentiality of hydrothermal basin's wastewater treatment using combined methods of coagulation and ozonation;

3) to evaluate potentiality of derived coagulate to increase an ability of sorbtion of adsorbent on clay's basis.

The objective of research and tasks

1) to analyse the literature data on the issue of modern approach to the wastewater treatment from HLES impurities. To summarize the theoretical and practical data on coagulation and ozonation methods. To analyse information about aluminium-containing composition coagulants;

2) to get model wastewater, which by chemical characteristics imitated hydrothermal basin's wastewater of plywood industry;

3) to study HLES components sedimentive stability and coagulation patterns from model wastewater in the wide pH environment and aluminium salts (aluminium sulphate, aluminium chloride, polyaluminium chloride, composition coagulants on polyaluminium chloride base) dosage range;

4) to develop a new composition coagulants on polyaluminium chloride base in order to remove hemicellulose and lignin-containing substances;

5) to study the efficiency of the remaining HLES degradation in the filtrate in the process of ozonation by pre-treating model wastewater with aluminium-containing coagulants;

6) to describe HLES coagulate, which occure due to the coagulation process by using new composition coagulants;

7) to modify Latvian clays with the coagulate and assess the ability of water adsorption by the derived sorbent, and its avalability to bind oil products and ions of heavy metals;

8) to offer a technological treatment sheme for wastewater treatment from hydrothermal basins and to carry out an economic assessment of proposed technology.

Scientific novelty and application

The scientific novelty of the Doctoral thesis is associated with the research of specific HLES removal during the process of coagulation using principally new composition coagulants on the base of polyaluminium chloride. The advantages of the developed composition coagulants compared to the traditional aluminum salts were presented.

In the course work the optimal technological parameters for wood origin pollutants removal in a process of coagulation using aluminium-containing coagulants were found. Performed laboratory studies allow to justify an effect of aluminuim salts on the HLES components sedimentation stability in water solutions.

The proposed wastewater treatment technology, that combines coagulation and ozonation processes, provides a high efficiency of wood origin pollutants removal. The developed combined method might be implemented in a plywood production cycle in order to re-use water for technological needs. The obtained by-products - coagulates, arising in a process of coagulation, is proposed to use for production of clay-based sorbents. The given fundamental results of the study might be used as a basis for products reworking, generating new and efficient materials.

Approbation

The results shown in this thesis has been reported and discussed in 16 international meetings.

The results shown in this thesis has been published in 8 full text scientific articles, 1 Latvian Republic patent and 11 scientific conference's thesis.

Full text scientific articles:

1. Shulga G., **Brovkina J.,** Skudra S., Shakels V., Belkova L., Cazacu G., Vasile C., Nita L. Self-organization of birch lignin and its aqueous solution properties// Proceedings at the EWLP 2010 - 11th European Workshop on Lignocellulosics and Pulp. - Hamburg, Germany. – 2010. - August 16-19. – 144.-148. p.
2. **Brovkina J.,** Skudra S., Šakels V., Šuļga G., Ozoliņš J. Choice of parameters for the model process simulating hydrothermal treatment of birch wood in veneer producing// Scientific Journal of Riga Technical University "Material Science and applied Chemistry". – 2010. – Vol. 22. – 140.-143. p. *(EBSCO, CSA/ProQuest, VINITI, Chemical Abstracts)*
3. **Brovkina J.,** Shulga G., J. Ozolins. Recovery of lignin and extractive substances from the hydrolysate of model birch wood hydrolysis with aluminium salt// Chemical Technology. – 2010. – Vol. 3-4(56). – 30.-34. p. *(Chemical Abstracts (CAplus))*
4. **Brovkina J.,** Shulga G., Ozolins J. Coagulation of wood pollutants from model wastewater by aluminium salts// Proceedings of the 8th International Scientific and Practical Conference Environment. Technology. Resources. - Rezekne, Latvia. – 2011. - June 20-22. – 63.-67. p. *(AGRIS)*
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7. **Brovkina J.,** Shulga G., Vitolina S., Neiberte B., Ozolins J., Turks M., Rjabovs V., Neilands R. Usage of coagulation with ozonation for treatment of model wastewater of wood processing with aluminium salts// CD-Proceedings of the 21st Century Watershed Technology Conference and Workshop Improving Water Quality

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8. Shulga G., Vitolina S., **Brovkina J.,** Neiberte B., Puķe M., Vedernikovs N., Turks M., Rjabovs V. Characterization of biomass from the wood hydrolyzate and its isolation with organic and inorganic polycation// Proceedings of the 12th European Workshop on Lignocellulosics and Pulp, EWLP-2012. – Espoo, Finland. – 2012. - August 27-30. – 512.-515. p.

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1. Shulga G., **Brovkina J**., Shakels V., Skudra S., Ozolins J. Composition and properties of lignin obtained by hydrothermal autohydrolysis of birch wood residue// Book of Abstracts of Baltic Polymer Symposium. - Ventspils, Latvia. – 2009. - September 22-25. – 90. p.

2. Shulga G., Shakels V., **Brovkina J.,** Skudra S., Neiberte B., Ozolins J. Viscosometrics and surface-active properties of lignin obtained by hydrothermal autohydrolysis of birch wood// Book of Abstracts of the 1st Symposium on Biotechnology Applied to Lignocelluloses. - Reims, France. – 2010. - March 28-April 1. – 127. p.

3. **Brovkina J.,** Skudra S., Shulga G., Ozolins J. Recovery of lignin compounds from the hydrolysate of model birch wood hydrolysis with aluminum salt// Book of Abstracts of Baltic Polymer Symposium. - Palanga, Lithuania. – 2010. - September 8-11. – 140. p.

4. **Brovkina J.,** Shulga G., Ozolins J. Influence of temperature on birch lignin coagulation with aluminum salts// Proceedings of the 6th meeting of the Nordic Baltic network in wood material science & engineering (WSE). - Tallinn, Estonia. – 2010. - October 21-22. – 103. p.

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Technology, Pharmacology, Medicine". - Saint-Petersburg, Russia. – 2011. - June 21-24. – 196.-197. p.

8. Shulga G., **Brovkina J.,** Skudra S., Neilands R. Wood processing wastewater treatment by coagulation and ozonation// Book of Abstracts of the Baltic Polymer Symposium. - Parnu, Estonia. – 2011. - September 21-24. – 39. p.

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11. Lakevičs V., **Brovkina J.,** Stepanova V., Dušenkova I., Ozoliņš J., Šuļga G., Bērziņa-Cimdiņa L. Using sorbents, developed on Latvian clay basis, in solving environmental problems// Book of Abstracts of the 17th International Conference "EcoBalt 2012". – Riga, Latvia. – 2012. - October 18-19. – 45. p.

Patent

1. Šuļga G., **Brovkina J.,** Neiberte B., Ozoliņš J., Neilands R. Methods for lignin and hemicellulose substances removal from wood processing wastewater// Latvian State Patent's claim P-12-115. Claim's publication to be present as consistent with Patent's law Section 35, Part 1, 20th of January, 2014.

LITERATURE REVIEW

The first Chapter "Composition of wood" characterized the wood components – cellulose, lignin, hemicellulose, extractive substances and lignin-carbohydrate complexes, their structure, functional composition and properties [5, 6].

The second Chapter "Production of plywood" describes the plywood manufacturing process and focuses on wood hydrothermal treatment. As a result, it was determined that wastewater contains the components of wood origin. Hemicellulose, lignin-containing compounds and wood extracts (HLES) are responsible for the high wastewater chemical oxygen demand value and the degree of coloration. There are no wastewater treatment plants in Latvia's plywood manufactory, therefore, this chapter identifies problems of the current water treatment processes and defines the objectives for future work.

The third Chapter "Wastewater treatment technologies for wood processing plants" describes the wastewater treatment methods, which have a widespread application in wood processing plants [7].

The fourth Chapter "Use of coagulation method for wastewater treatment" explains the nature of coagulation methods. This chapter summarises extensive information on the availability of the aluminium-containing and composition coagulants used on its base [8].

The fifth Chapter "Ozonation methods for wastewater treatment" contains information on the ozone interaction with organic compounds and ozonation method's implementation for wastewater treatment. It was found that ozonation provides treated water quality that meets this re-use [9]. The second work goal was formulated in this chapter.

The sixth chapter "Wastewater sludge" gathers the information, which allowed setting the third objective to the paper. It is rational not to consider the by-products formed during the wastewater treatment process as a waste but as a secondary raw material.

On the basis of analysis of literature review it is concluded that it is necessary to develop the wastewater treatment methods for hemicellulose and lignin-containing substances removal, that allows water return to the technological cycle, but the by-products can be used as a secondary raw materials in the national economy.

METHODS

The model wastewater with clear and stable characteristics was used in order to study the coagulation mechanisms of wood origin pollutants and factors that influence treatment effectiveness. A number of standard methods (COD, BOD_5, TOC, coloring and residual aluminum identification, etc.) as wood chemical analytical methods (determination of functional groups, etc.) and instrumental methods for structure identification (FT-IR, ^{13}C-KMR) were used to characterise sample liquid's HLES components.

Aluminium sulphate ($Al_2(SO_4)_3$), aluminium chloride ($AlCl_3$) and polyaluminium chloride (PAC) were used as nonorganic coagulants for removal of wood origin pollutants. The composition coagulant on a base of $Al_2(SO_4)_3$ and PAC (KSPAC) and developed a new composition coagulant on a base of PAC (KHPAC) with a various initial components content were used in the work. Two methods were used to characterise aluminium-based coagulants (Ferron's method and ESI-MS), that allowed to investigate the content and form of coagulant hydrolysis product.

The coagulation of model wastewater was carried out by mixing sample solution's coagulant in equal volumes. After 120 minutes of solution's treatment, it is filtered through a glass fiber filter, but the filtrate is analysed to determine: the total HLES content (spectrophotometric method at a wavelength of 490 nm), aromatic substances content (spectrophotometric method at a wavelength of 280 nm), PI, coloring, COD, TOC, BOD_5, the residual concentration of aluminum, chloride's and sulfate's content (LVS EN ISO methods) and so on. Coagulation efficiency was determined by comparing treated model wastewater early indicators with the parameters obtained in filtrate after coagulation.

The ozone generator (KH-AW-5A-2) with ozone-air mixture supply of 20 l/min and ozone concentration in a mixture of 0.6 mg/l was used in the ozonation process. The derived purified water was qualitatively analyzed using the above methodology. It also was analyzed on the content of organic acids, phenol and carbonyl compounds.

The granulometric and elementary composition of coagulate, derived in a process of coagulation by new composite coagulants, was determined. Coagulate was used as an active additive to Latvian clay deposits from Vadakste (LTM). The modification of clay was performed by loading the coagulate (1.8-1.9%) in the clay's granulas with the size of 0.25-3.0 mm by means of spraying. Modified samples were heat-treated at a temperature range of 300-800˚C. The derived clay materials were analyzed for the water capacity, water and oil sorption and linking of heavy metals.

RESULTS AND DISSCUSION

Characterization of the model wastewater

The obtained results show that the content of hemicellulose in the model wastewater varies from 75-80 %. The content of Klason lignin varies from 10 to 12%, lignin-hemicellulose complexes, low molecular aromatic products and hemicelluloses monomers varies from 10 to 15%. The products of aromatic nature are noted by LSV. The description of model wastewater is given in Table 1.

Table 1.

The characteristic of the model wastewater

Parametrs	Value
HLES, mg/l	1400
LSV, mg/l	280
Colority, mg/lPt	746
COD, mgO/l	1285
PI, mgO/l	320
BOD_5, mgO/l	88
TOC, mg/l	732
Phenol index, mg/l	0.24

The derived model wastewater (MW) by its chemical characteristics had imitated plywood manufacturing hydrothermal basin's wastewaters (NW), as it was evidenced by the derived FT-IR spectra and elementary composition analysis.

Characterization of the aluminium salts

In order to determine quantities of the aluminium monomeric and polymeric forms in all types of coagulants the Ferron method was used. The method is based on interdependent monomers, polymers and high molecular weight aluminium forms of reaction kinetics with Ferron reagent [10]. The obtained results are summarized in Table 2.

Table 2.

The Al speciation distributions of $Al_2(SO_4)_3$, $AlCl_3$ and PAC

Coagulants	Al_a, %	Al_b, %	Al_c, %
$Al_2(SO_4)_3$	90.3	9.7	0.0
$AlCl_3$	67.5	32.5	0.0
PAC	16.6	66.6	16.8

Al_a - monomeric species; Al_b - mediumpolymer species; Al_c – large polymeric or solid species

In the result of interaction of the aluminium salts with reagent, the coloured complexes, the optical density of which at 370 nm is measured in time, have appeared. Monomeric aluminium forms (Al_1) with Ferron reagent react within 1 minute, polymer aluminium forms (Al_2-Al_{10}) with Ferron reagent reacts within 120 minutes, but the high molecular forms and amorphous aluminium phase (Al_{11}-Al_{21}, $Al(OH)_3$) react slowly or do not respond at all. From Table 2, it can be seen that the Al speciation depends on the aluminium salts types. For $Al_2(SO_4)_3$ the main species is Al_a, $AlCl_3$ contains Al_a and more Al_b than $Al_2(SO_4)_3$. For PAC the major Al species are mediumpolymeric Al_b and polymeric forms with large number of Al.

Coagulation of wood origin pollutants with aluminium salts

The experiments were conducted at 3.0-10.0 pH range with coagulants doses of 25-850 mg /l, at the temperature of 13-40 (±1)˚C. Assessing the results obtained, it is determined that the optimal pH value areas for HLES coagulates formation, which has a high filtering properties, are pH 5.0-6.0 for $Al_2(SO_4)_3$, 6.0-7.0 for $AlCl_3$ and PAC. The pH value determines not only the HLES removal mechanism and efficiency, but also the residual aluminium concentration in the system after coagulation and filtration. The minimum residual aluminium concentration corresponds to a pH range of 5.0-7.0. The selection of optimal coagulant doses at a particular pH values is measured by several criteria: HLES removal high efficiency (≥80%), low residual aluminium concentration and reagent's saving. From the technological point of view, the optimal coagulant dose is being considered as a dose, at which the following coagulant's injection does not supply HLES removal efficiency's increase by 5%. The model wastewater treatment's efficiency was determined by using $Al_2(SO_4)_3$, $AlCl_3$ and PAC (Fig. 1.), taking into consideration the optimal pH value and relevant optimal doses.

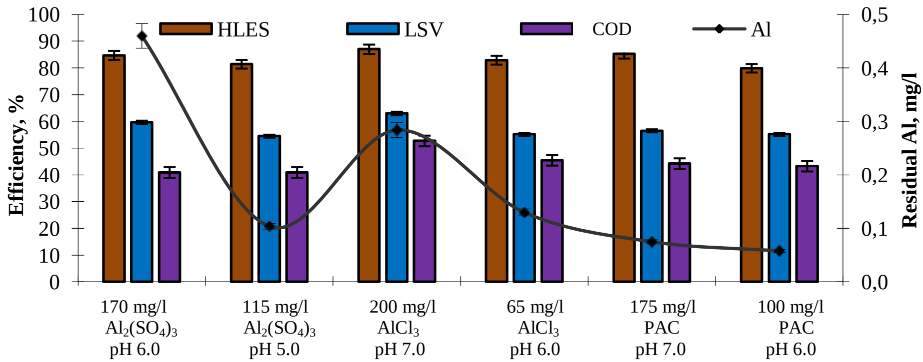

Fig. 1. Efficiency of model wastewater treatment at the optimal conditions

Based on the outcomes, it can be concluded that model wastewater eliminating efficiency of HLES components in the excerpted conditions is commensurable. HLES removal makes up to 80-86%, LSV - 53-60%, COD - 40-50%. In turn, having analysed the residual aluminium concentration in the filtrate after treatment, it was found that while using PAC the increase of dose from 100 to 175 mg/l practically has no effect on the residual aluminium concentration and it is characterized by lower values (0.07-0.09 mg/l) compared to traditional aluminium salts. Coagulates, which are formed in the presence of PAC precipitate and densify much faster compared to $Al_2(SO_4)_3$ and $AlCl_3$.

It can be concluded that the for $Al_2(SO_4)_3$ and $AlCl_3$, HLES, LSV, COD value decline occurs more intensively at raised temperatures, while studying the effect of temperature on HLES removal efficiency. The temperature's decrease from 20°C to 13°C caused wood origin pollutants removal efficiency's deterioration by an average of 24%. The residual aluminium concentration increased to 2-3 times. Use of PAC shows an unequivocal advantage at a low temperatures compared to $Al_2(SO_4)_3$ and $AlCl_3$. The eliminating efficiency of sample liquid in the presence of PAC at temperatures of 13 and 20˚C is comparable; moreover, the residual aluminium concentration does not change and makes up to an average of 0.07 mg/l.

Coagulation of wood origin pollutants with composite coagulants

Based on the results, the task was to increase the treatment efficiency of wastewater, that contain pollutants of wood origin, and to develop conditions of treatment methods by coagulation.

It was concluded from the experimental data that the PAC has the highest activity, as it is characterized by:

o relatively small optimal dose (100 mg/l);

o low residual aluminum concentration in the treated water;

o insensitivity to temperature changes;

o better sedimentation kinetics.

Based on the data of aluminium-containing coagulants costs, in accordance to prices, given salts may be placed as follows: $Al_2(SO_4)_3 < AlCl_3 <$ PAC. On that basis, one of the purposes of the present thesis was the development of composition coagulant on the PAC base. Composition coagulant must meet the following criteria: it should be able to reduce consumption of PAC, efficiency should be commensuarable or better than the PAC and valuable technological properties of PAC should be kept. In the course of the work the new composition coagulant on the basis of PAC was developed (KHPAC). The invention is patented [11]. As a prototype of proposed invention, the composition coagulant on PAC and $Al_2(SO_4)_3$ bases was selected (KSPAC) [8]. The PAC content varied in composition coagulants.

Data for efficiency of HLES removal depending on the composition coagulant KHPAC and temperature are shown in the Table 3. Two optimal compositions $KHPAC_{40}$ and $KHPAC_{50}$, that ensures maximum efficiency of HLES removal (> 86%), insensibility to changes in temperature and sufficiently large PAC replacement (50-60%), were selected.

Table 3.

Efficiency of HLES removal depending on KHPAC composition and temperature. Dosage - 100 mg/l, pH treatment - 6.0

Composition	Temperature		
	13°C	20°C	40°C
	HLES removal efficiency, %		
$KHPAC_{90}$	91	92	88
$KHPAC_{50}$	92	95	88
$KHPAC_{40}$	86	92	88
$KHPAC_{30}$	78	76	78
$KHPAC_{20}$	77	75	74
$KHPAC_{10}$	77	85	85

Figure 2. shows the removal efficiency of wood origin's pollution depending on the pH values of the system, using $KHPAC_{50}$ and PAC dosage of 100 mg/l.

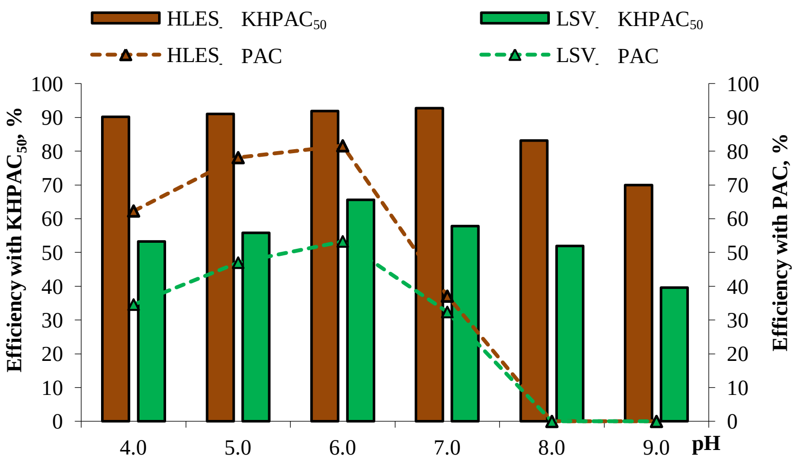

Fig. 2. Effects of pH on HLES removal with $KHPAC_{50}$ and PAC (100 mg/l)

The results are compared with the efficiency achieved using the PAC under the same conditions. The usage of $KHPAC_{50}$ composition coagulants expands the pH value, where HLES efficient removal from model wastewater was obtained. $KHPAC_{50}$ compelling advantage is observed at pH 4.0 and in area 7.0-9.0. In order to remove HLES from model wastewater at maximum, pH range has to be 5.0-7.0. Taking into consideration the residual aluminium concentration in the system, which is equal to 0.759, 0.074 and 0.127 mg/l, respectively, it is recommended to take the optimal pH value of 6.0-7.0. At pH 6.0 and 7.0 HLES removal efficiency increases to 12% and 50%, LSV to 14% and 25%, respectively, compared to PAC.

Optimal dosage of PAC at pH 6.0 is 100 mg/l. An interest was caused by study of influence of dose on efficiency of model wastewater treatment at pH 6.0 in the presence of $KHPAC_{50}$ (Fig. 3). The experiments with $Al_2(SO_4)_3$/PAC composition coagulants were made. The content of PAC in composition coagulant was 50%.

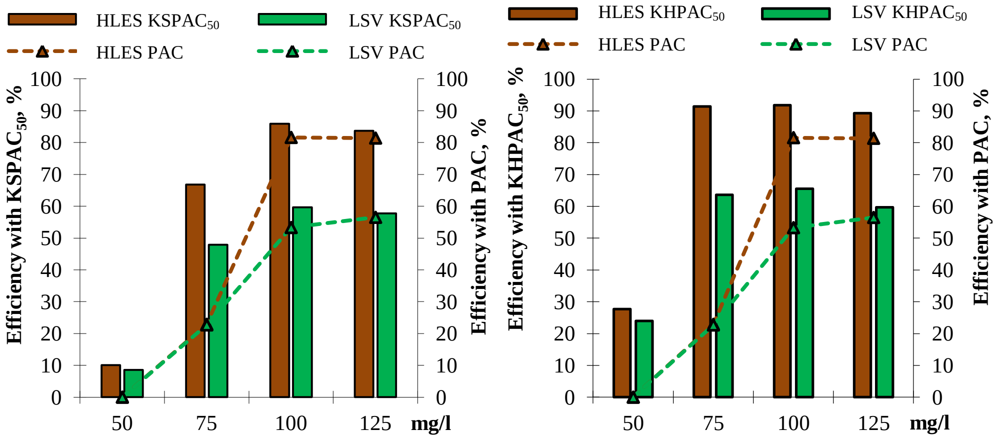

Fig. 3. Effects of $KSPAC_{50}$, $KHPAC_{50}$ and PAC dosage on HLES and LSV removal (pH 6.0)

It is necessary to mention the incontestable $KSPAC_{50}$ and $KHPAC_{50}$ composition coagulants advantage for PAC in all dose range studied (Fig. 3). The given results show that the optimal dosage of $KSPAC_{50}$ is 100 mg/l, the efficiency of HLES removal is 86% and removal of LSV is 60%. Coloration decreased to 84%, but the residual aluminum concentration is equal to 0.168 mg/l. In turn, $KHPAC_{50}$ optimal dosage is 75 mg/l. HLES removal efficiency amounts to 91%, removal of LSV to 64%. Coloration decreased to 89%, but the residual aluminum concentration is equal to 0.092 mg/l. At a dose of 75 mg/l $KHPAC_{50}$ HLES and LSV removal efficiency increases by 68% and 41% compared to the PAC, by 26% and 15% compared to $KSPAC_{50}$.

Increase of coagulation's ability to new composition coagulants in relation to PAC as well as coagulant on the prototype had occurred due to the fact, that KHPAC system were forming mostly multi Al-complexes, which have polymeric and high molecular structure. It is proved by comparative study of composition coagulants by means of using Ferron's method and electrospray ionization mass spectrometry [12]. Composition coagulant $KSPAC_{50}$ is characterized by presence of monomer $[Al(OH)_2(H_2O)_{1\text{-}2}]^+$, dimer $[Al_2O_2(OH)(H_2O)_{0\text{-}4}]^+$, trimer $[Al_3O_4(H_2O)_{0\text{-}5}]^+$, tetramer $[Al_4O_5(OH)(H_2O)_{1\text{-}5}]^+$ and pentomer aluminium $[Al_5O_7]^+$ form's signals, as well as high molecular weight form of aluminium $[Al_{13}O_{18}(OH)(H_2O)_{0\text{-}4}]^{2+}$. In turn, the presence of high molecular form $[Al_{12}O_{17}]^{2+}$ and $[Al_{14}O_{20}(H_2O)_{0\text{-}1}]^{2+}$, without specified aluminium monomeric and polymeric forms of aluminium, is explicit to composition coagulant $KHPAC_{50}$. The signals featured to high molecular forms of aluminium forms with 16 aluminium atoms in structure were observed in case of $KHPAC_{50}$.

The method of ozonation as a second stage in treatment of wood origin pollution

Taking into account a goal of water re-use set, it was necessary to choose a second treatment stage, which would be effective, fast and does not require use of chemical reagents. The method of ozonation was chosen for this task.

Ozonation was used for filtrates derived as a result of sample liquid's treatment with 100 mg/l of aluminium-based coagulants at pH 6.0. Using an ozone generator with an ozone-air supply of 20 l/min and ozone concentration of 0.6 mg/l in a mixture, from a technological and economic point of view the time range of 30-60 minutes may be taken as an optimum period of ozonation.

Using $KHPAC_{50}$ coagulant in the first stage and ozonation in the second stage, the following indicators were achieved: HLES removal - 99%, LSV - 94%, TOC - 92%, BOD_5 - 95%, coloration - 97%. Table 4. shows complete characteristics of sample before and after use of the combined treatment methods.

The results show the high degree of model wastewater treatment. The sample quality indicators enclosed within the threshold interval defined for natural waters with a view to use them as an industrial water. However, it should be noted that the COD ratio in the outgoing flow after ozonation is quite high 144 mgO/l. This is associated with organic acids and carbonyl compounds formation. From the identified range of aldehydes and ketones the greatest concentration belongs to formaldehyde (0.47 mg/l), which in turn does not exceed the maximum allowable limit (1.0 mg/l). Other compounds such as acetaldehyde, acetone, butanal and others vary at the range of 0.01-0.04 mg/l. It was found that volatile organic acid content comes up to 46.5 mg/l.

Table 4.

Model wastewater quality before and after treatment by coagulation and ozonation methods

Parametrs	Value				LS Water quality norms	
	Input wastewater	Control wastewater	Wastewater after coagulation	Wastewater after ozonation	Aim value	Limit value
HLES, mg/l	1400	700	33	9	Non-regulate	
LSV, mg/l	280	140	53	6	Non-regulate	
COD, mgO/l	1285	660	367	144	30 [2]	300 [3]
Colority, mg/lPt	746	501	60	16	50 [2]	200 [2]
TOC, mg/l	732	360	123	28.6	Non-regulate	
BOD_5, mg/l	88	58	18	3.2	<7 [2]	Non-regulate
Al, mg/l	---	---	0.061	0.203	Non-regulate	0.5 [2]
SO_4^{2-}, mg/l	---	---	6.93	2.10	150 [2]	250 [2]
Cl^-, mg/l	---	---	37.2	35.1	200 [2]	Non-regulate
NO_3^-, mg/l	---	---	---	22.3	Non-regulate	50 [2]
NO_2^-, mg/l	---	---	---	<0.01	Non-regulate	0.5 [2]
Phenol index, mg/l	0.24	---	0.08	<0.02	0.01 [2]	0.1 [2]
Volatile organic acid, mg/l	---	---	---	46.5	Non-regulate	
Formaldehyde, mg/l	---	---	---	0.47	Non-regulate	1.0 [4]
pH	9.02	8.1	5.9	3.9	5.5-9.0 [2]	
Conductivity, (µS/cm)	787	440	498	514	1000 [2]	Non-regulate

[1] Coagulation is carried out by mixing the incoming flow of coagulant solution in the ratio 1/1. Efficiency is calculated in regard to control flow in order to avoid effect of dilution.

[2] Annex 6 of the Ministers Cabinet's regulations No. 118 of 12th March 2002 - Water quality standards for production of drinking water used for the surface waters in accordance to their division in categories.

[3] Annex 10 of the of Ministers Cabinet's regulations No. 118 of 12th March 2002 - Water quality standards for the assessment of groundwater state, as well as the requirements for the groundwater treatment in the contaminated areas.

[4] Annex 1 of the of Ministers Cabinet's regulations No. 118 of 12th March 2002 - Priority and hazardous substances environmental quality standards for surface waters, as well as priority substances environmental quality standards for surface waters biota organisms.

Fig. 4. The model wastewater (a), filtrate after coagulation (b), after ozonation (c)

Characteristics and usage of derived coagulate

Coagulate HLES-Al, obtained while treating model wastewater with $KHPAC_{50}$ at pH 6.0, is characterized by high moisture - 98.2%. Studying the coagulate's granulometric speciation, it has emerged that the size of particles varies form 2 to 246 μm, but an average size is equal to 45.8 μm. The derived coagulate composed primarily of carbon (27.9%), oxygen (49.4%) and aluminum (10.9%). The qualitative composition of the HLES coagulate was defined by using ^{13}C-NMR spectroscopy. It is concluded that the existing hemicellulose in the HLES-Al coagulate is characterized by O-acetyl-4-O-methyl-D-glucuron-β-D-xylan with β-(1-4)-glucomannose.

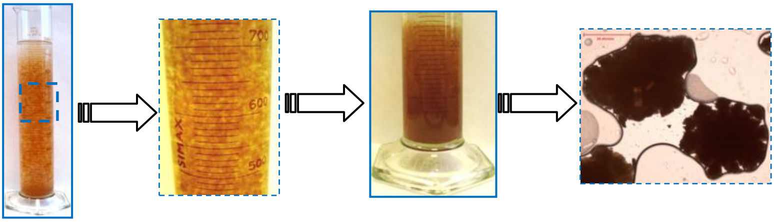

Fig. 5. HLES- Al coagulate

Bearing in mind that in the proposed technology of hydrothermal basin water treatment the given coagulate is a waste of large-tonnage, the issue of its liquidation or recirculation is very topical. Reasoning from this fact, in the frame of this scientific work, the aim was set to assess the feasibility of the given coagulate. On the basis of literature data, it was selected to give a trial to the use of coagulate for clay sorbents' production.

Latvian clays from Vadakste deposits (LTM), and model wastewater coagulate with a concentration of 1.8-1.9% were used as a research object. Treating clay with coaguate, it was determined that, firstly, fractional composition of the clay was changing. The clay coagulates' content of 0.05% dry matter, the large fraction content with a diameter > 3.0 mm in relation to control would be increased twice.

The second stage of analysis was associated with study of lifting capacity of water, water and oil binding capacity of initial and modified clay. Two processes were considered in the course of work: water capacity and water-binding capacity. The first technique is based on the study of unmodified and modified clay's ability to absorb water, taking into account the limited water - clay contact. The second technique is characterized by entire water - clay contact.

According to the results obtained, the optimum carrying capacity of water is peculiar to the LTM 011 (the optimal content of coagulates in clay - 0.11%) samples with fraction size of 2.0-3.0 mm and amounted to 740 mg H_2O/g, which is about 35% more in point of initial LTM. Conversely, the water-binding capacity depends on the time. LTM and LTM 011 samples saturation occurs within the first 4 minutes. Water binding capacity of LTM 011 sample is up by 35% and 11% compared to the LTM samples within 1 and 4 minutes contact time, respectively.

The rapeseed and silicone oils were used for the oil-binding studies. Samples saturation occurs within 10 minutes. Rapeseed oil and silicone oil sorption concerning LTM 011 sample is higher by 31% and 21% respectively, compared to LTM and is equal 520 and 428 mg/g, respectively.

LTM and LTM 011 clay samples' heat treatment occurred at the temperatures of 300, 500 and 800˚C. It is found that increasing temperature up to 800˚C, it has resulted in significant decrease of LTM and LTM 011 activity in relation to water (Fig. 6). Clay samples sorption capacity's reduction in relation to water is due to the fact that the heat treatment causes clay's hydrophobicity and contributes to less-developed texture (Fig. 7.).

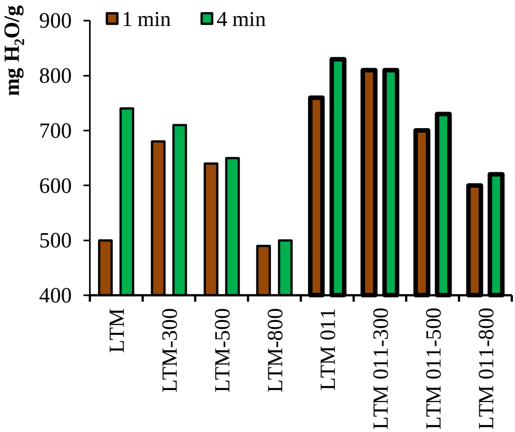

Fig. 6. The heat treatment effect on water binding capacity of LTM and LTM 011 samples

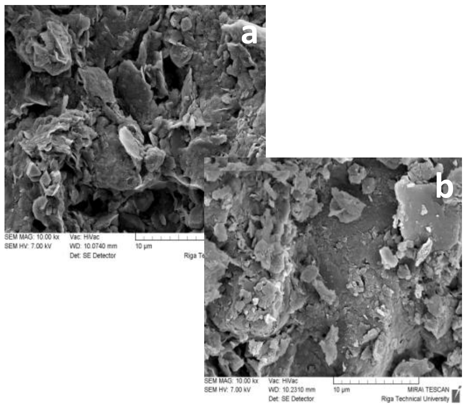

Fig. 7. LTM 011 (a) and LTM 011-800 (b) samples SEM microphotographs

It is necessary to emphasize that the LTM 011 sample's water-binding capacity within 4 minutes is up by 11-19% compared to the LTM sample's water-binding capacity, regardless of the heat treatment temperature.

By studying the oil-binding capacity of LTM and LTM 011 samples, it was found that the oil sorption increases as the clay sample's treatment temperature increases (Fig. 8.). It should be noted, that the modified clay cured at 800°C, silicon and rapeseed oils binding capacity is by 22% and 30% higher compared to the LTM-800 sample.

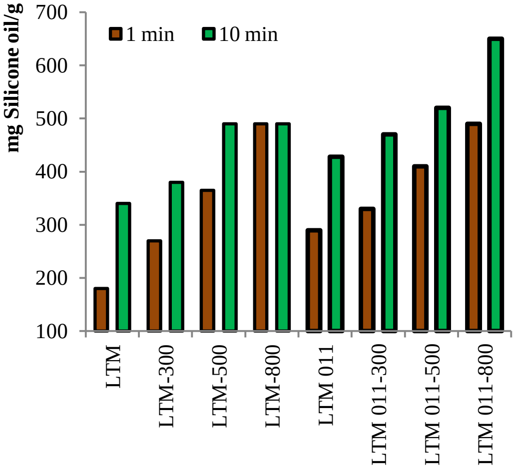

Fig. 8. The heat treatment effect on oil binding capacity of LTM and LTM 011 samples

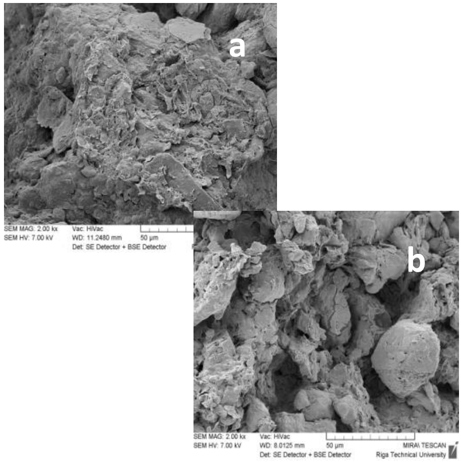

Fig. 9. SEM micrographics of the fracture surface of LTM-800 and LTM 011-800 samples

Treating clay with coagulate, the organic-mineral structure has formed, which loses an organic part at the thermal treatment as a result of combustion, but retains the developed structure in the inner part, as evidenced by the LTM-800 and LTM 011-800 SEM microphotographs (Fig. 9).

The ability to adsorbe copper and zinc ions from aqueous solutions by initial and modified clay samples was studied. Samples cured at 800°C in order to increase the sample hydrophobicity were used. Determination of the metal's concentration in aqueous solutions before and after the use of clay samples was carried out by atomic-absorption method. It was found that LTM-800 sample reduces the zinc ion concentration of the solution by 60%. While the LTM 011-800 sample by 72%. Removal of copper ions was 65% and 75%, respectively of LTM-800 and LTM 011-800 samples. LTM 011-800 sample shows higher sorption activity for heavy metals compared to the LTM-800 sample.

The results of study enable to suggest that many tons of waste that will be produced in the as a result of plywood industry 's wastewater chemical treatment, can be processed into valuable products on a clay basis that can be used as water, oil and heavy metals sorbents, as well as adsorbing filler production.

Treatment scheme for plants processing wastewater polluted by woody tissue

The proposed technology in this work is the optimal model and the resolution that can be actualized in the production level. The technology is being implemented in four stages (Fig.10).

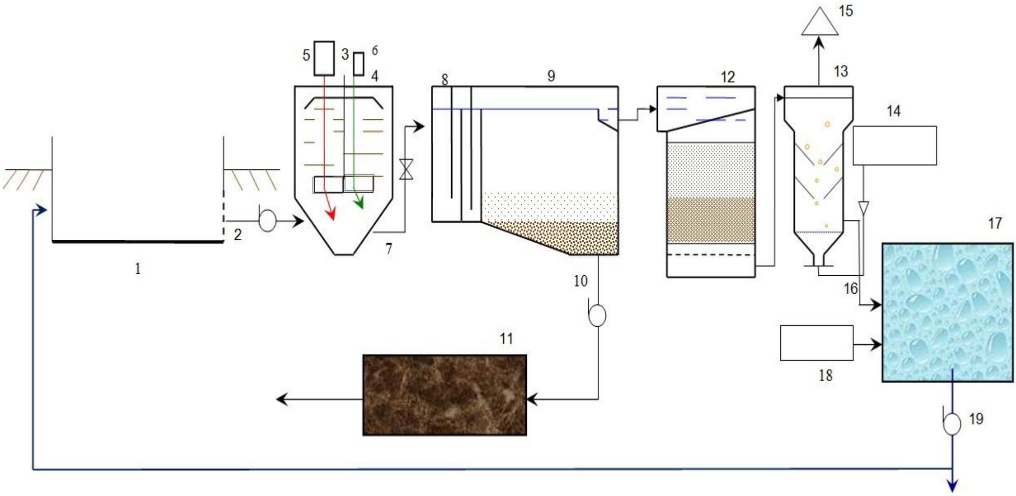

Fig. 10. Technological scheme of hydrothermal basin wastewater treatment:
1 - hydrothermal pool, 2 - coarse and fine grids, 3 - mechanical stirrer, 4 - mixing tank, 5 - coagulant dispenser, 6 - alkaline (acid) dispenser, 7 - pipeline, 8 - flake producing chamber, 9 – filter bed, 10 - sediment removal wire, 11 - sludge tank, 12 - filtration tank, 13 – ozonation plant, 14 - generator of ozone, 15 - ozone decomposer, 16 - purified water pipeline, 17 - purified water reservoir, 18 - alkaline tank and dispenser, 19 - purified water pump

The first stage is based on hydrothermal basin (1) wastewater circulation through the grille (2) in order to detain floating pollutants of considerable dimensions.

The second stage is performed with a water treatment coagulation method. Firstly, wastewater and reagent mixing is happening in mixing machine (3). Mixing of coagulants and water the bladed and propelling mechanical stirrer is used (4). Coagulant is being dosaged through the use of coagulant dispenser (5). Using the composition coagulants, it is necessary to use a fractional coagulation, which provides the reaction of coagulants’ addition to water in the following two portions. Reagents are added for pH correction through the dispenser (6). After mixing the wastewater with coagulants the process of flakes development begin. The pipelines (7) retrieve water from stirrer to the flake producing chambers (8). After passing through the flake producing chamber, the wastewater flows directly into the sedimentation tank (9). Exploiting the sedimentation tank, it is necessary to keep up with sediments levels.

Precipitation is recommended to separate by means of hydraulic (10) and remove them specifically for the sludge tank (11) on a regular basis. Water has to be located in the sedimentation tank for 40-60 minutes

After sedimentation, the purified stream is delivered to the third treatment – filtration (12). In the given technological scheme, the filtration procedure was a stage, which prevents the non sediment coagulate into the reactor, where the ozonation takes place. The filtrate is delivered to the contact chamber for ozonation (13). Ozone-air mixture (14) is injected by means of the pipes from a porous ceramic. Ozone-air mixture leaving the contact reactor goes to the ozone decomposer (15). The release of ozoned water is carried along the line (16) to the receiving tank (17), where purified water's pH is strictly controlled and added to the caustic alkali as needed to achieve pH 6.0 (18). To control the quality of the water flow samples are periodically taken from the reservoir for analysis. Purified water is supplied to the hydrothermal basins.

The calculations, that allow assessing the cost of technology maintenance within a year, were made for proposed technology. It was assumed that in the process of coagulation composition coagulant $KHPAC_{50}$ was used. Wastewater treatment was carried out at pH 6.0. Wastewater delivery to the treatment plants at 30 m^3/h (720 m^3/day). The following factors were taken into account while performing calculations: the expenses for the reagents procurement and transportation, customs duty and value added tax, consumption of water, consumption of electricity for making coagulant's solution and mixing with wastewater, pumping, filtration and ozone generation and so on. The calculations of cost of the wastewater discharge into the city drainage, taking into account the regulations of Riga City Council and costs associated with compensation of hydrothermal basin's discharged water, were made. It was found that the company's financial benefit amounts to approximately 34% of the sum that could be spent in case of wastewater discharge into the city drainage.

CONCLUSIONS

The course of work is devoted to removal of the wood pollutants from the wastewater, that arises in the mild process of wood hydrolysis, using combined methods of coagulation and ozonation processes. The following conclusions are made:

1. The optimal conditions for model wastewater obtaining were chosen. The derived model wastewater imitated the wastewater from plywood industry of hydrothermal basin.

2. In the process of studying the removal efficiency of the wood pollutions, using the method of coagulation with aluminium salts, it is determined that the optimal environmental pH range is 5.0-6.0. The adjustment of pH value can be considered as an additional measure to coagulation effectivization.

3. In terms of efficiency of wood pollutants removal, aluminium salts may be arranged in the following order: $Al_2(SO_4)_3$ < $AlCl_3$ < PAC. An advantage of polyaluminium chloride regarding aluminium sulphate and chloride is high efficiency at low temperatures and low residual aluminium concentrations in water after treatment.

4. Using of composition coagulants $Al_2(SO_4)_3$/PAC with the PAC replacement on 50%, efficiency of the wood pollutants removal increases by an average of 18% for $Al_2(SO_4)_3$ and 12% for PAC.

5. The new composition coagulant on the basis of polyaluminium chloride base was developed. The composition coagulants’compound provides 50-60% polyaluminium chloride substitution with cheaper reagent. $KHPAC_{50}$ optimal dose was for 25% smaller than the PAC and $Al_2(SO_4)_3$/PAC dose. Under the optimal dose of developed composition coagulant, HLES and LSV removal efficiency was increased by 68% and 41% compared to the PAC, and by 26% and 15% compared to $KSPAC_{50}$. Higher efficiency of the developed composition coagulant is related to the diversity of products of aluminium hydrolysis and presence of high-polymeric aluminium form, which is not indicative to aluminium salts and composition coagulant $Al_2(SO_4)_3$/PAC. The usage of composition coagulant increases the working pH range, and it is being characterised by low residual aluminium concentration and insensitivity to temperature changes.

6. The results of studies have shown high efficiency of separation of the remaining hemicellulose and lignin-containing substances after use of the coagulation during the ozonation process. The total treatment efficiency exceeds limit of 92%. It is found that for 1 mg TOC removal is necessary 3.8 mg of O_3. The qualitative speciation of outflow corresponds to the water re-use in technological cycle.

7. The derived coagulate composed primarily of carbon (27.9%), oxygen (49.4%) and aluminum (10.9%). It is concluded that the existing hemicellulose in the HLES-Al coagulate is characterized by O-acetyl-4-O-methyl-D-glucuron-β-D-xylan with β-(1-4)-glucomannose.

8. Coagulates produced in the process of coagulation with use of new composition coagulants increases the sorption activity of Latvian clays. The optimal dry coagulates speciation of clay forms 0.11%. Modified clay sorption capacity for water will increase by 35%, while for the rapeseed and silicone oil, compared to the raw clay, is 31 and 21%, respectively. Linking of heavy metals is increased by 12%.

9. The local treatment scheme was elaborated and created for wastewater treatment from wood pollutants. The proposed method is characterized by an economic advantage, compared to the equivalent amount of water released in a central sewerage system.

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