The Colloidal Stability of Wood Originated Pollutants in the Presence of Aluminium Salts

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***Abstract*: Latvia is the biggest producer of plywood in Eastern Europe. One of the stages of raw material preparation is hydrothermal treatment of birch wood. Wastewater from plywood hydrothermal basin is characterized by the high degree of contamination. The basic contaminating components of this wastewater are lignin, hemicellulose and extractives of wood (LES), which are the main reason of a high level of chemical oxygen demand (COD) and color of water. The aim of this work is to find out the regularity of coagulation of LES with inorganic coagulants – aluminium salts in the wide range of pH and concentrations. The efficiency of LES coagulation was defined after 2 hours of the system settling and filtration. The colloidal stability and coagulation of LES in the presence of aluminium salts was studied by spectrophotometry method. It is set that at the use of $Al_2(SO_4)_3$ with an optimal dose 115 mg/l and pH environment 5.0, LES educing is 81.4%. An optimal dose and pH for $AlCl_3$ are 65 mg/l and 6.0, and here the LES educing is 82.8%. In the presence of PACl with an optimal dose of 100 mg/l and pH environment 6.0, LES educing is 79.8%. Efficiency of coagulation method is regulated by the dose of coagulant and pH environments. Correct choice of these parameters can substantially intensify the process of wastewater of hydro basin of plywood production purification based on the method of coagulation.**

***Keywords*: coagulation, aluminium salts, lignin, hemicellulose, colloidal stability**

I. Introduction

The problems of environment protection and rational use of natural resources remain the issues of the contemporaneity. The main problem of the plywood industry enterprises is wastewater cleaning and development of the maximally repeated water consumption. From the other side, low-molecular compounds that emerge as a result of wood hydrothermal treatment, can be of interest for obtaining adhesives and functional additives for composite materials [1, 2].

One of the stages in the preparation of raw material for plywood production is the hydrothermal treatment of birch wood. Wastewater from plywood industry of hydrothermal basin is characterized by the high degree of contamination as it contains wood originated pollutants – low-molecular fragments of lignin, hemicellulose and extractive of wood (LES). Even the most advanced technologies do not allow to utilize these co-products entirely, and they remain in wastewater in significant quantity that gives them the specific colouring and high value of chemical consumption of oxygen (COD). LES present a considerable danger for the ecosystems of natural aquatic objects, because they are direct contamination source that is related to the change of their colloid-chemical state in the aquatic systems. Streams containing LES create considerable difficulties in the traditional methods of biological purification and require the additional stage of physical and chemical treatment (coagulation) providing fault norm, and also possibilities of return of them in the main technological cycle. Problem solving related to the development of excrete methods of LES components from wastewater is impossible without fundamental researches of their colloid-chemical behavior in aquatic systems.

The aim of this work is to find out the regularity of coagulation of LES with inorganic coagulants – aluminium salts in the wide range of pH and concentrations.

II. Materials and Methods

The birch wood sawdust was used for the wood hydrothermal treatment. A hydrolysis was fulfilled in an alkaline water environment at the water duty of 1/50, the temperature 90°C and the duration was about 4 hours [3]. Model solution was brown colored (746 mg/lPt), alkaline with pH 8.9-9.2. The model solution contains higher concentration of COD (1285 mgO/l) and dissolved solids (1400 mg/l).

Aluminium sulfate ($Al_2(SO_4)_3$), aluminium chloride ($AlCl_3$) and polyaluminium chloride (PACl) were used as coagulants and the working solutions were prepared by dissolving the coagulant in distilled water depending on the dose required. The process of coagulation was performed by mixing equal volumes of the coagulant and model solutions. The optimal terms of the LES removal in the presence of aluminium salts were studied, varying the concentration of coagulants from 15 to 850 mg/l. The pH value of the mixed systems was adjusted to a pH 10.0–3.0 by using 1.0 M NaOH and HCl.

The efficiency of LES coagulation was defined after 2 hours of the system settling and filtration. The colloidal stability and coagulation of LES in the presence of aluminium salts was studied by spectrophotometry method. The residual concentration of LES in the filtrate was defined by measuring filtrate optical density (*A*) at the wavelength 490 using the preliminary received correlation curves. The filtrate color was defined by the method of photometry at the wavelength of 436 nm; the results were reported in platinum-cobalt (PtCo) units (ISO7887:1994). COD was determined by the oxidization of the received filtrate by adding potassium dichromate under the given reaction conditions (LVS ISO 6060:1989).

III. Results and disscusions

Initial model solution is sedimentation-steady in pH area from 3 to 10. During the coagulant uptake the system loses the aggregate stability. Table I presents the results reflecting the values of critical concentration of coagulation (minimum concentration of coagulant, at which rapid coagulation takes place) of $Al_2(SO_4)_3$, $AlCl_3$ and PACl depending on the value of pH, at which the process of LES coagulation was accomplished.

TABLE I

CRITICAL COAGULATION CONCENTRATION (C.C.C.) OF ALUMINIUM SALTS ADDED TO THE MODEL SOLUTION DEPENDING ON THE PH OF THE MIXED SYSTEMS

pH of mixed system	(C.C.C.) of aluminium salts in model solution		
	$Al_2(SO_4)_3$, mg/l	$AlCl_3$, mg/l	PACl mg/l
10.0	680	650	150
9.0	350	300	150
8.0	136	85	150
7.0	125	50	125
6.0	125	50	100
5.0	50	39	75
4.0	60	39	50
3.0	68	39	50

It is seen from the presented results that at a lower value of pH, critical concentration of coagulation is lower than in alkaline environments. According [4], the change of the pH system causes the change of density size of negative surfaced charge of LES particles, thus the system loses stability as far as approaching to the point of a zero charge of these components, which testifies to the neutralization mechanism of coagulation. At a high pH level LES is well soluble, thus their removing with aluminium salts in the process of coagulation is difficult, that is related to the increase of numbers of the ionized groups in the particles of these matters and strengthening of their hydrophilic properties.

Efficiency of LES removal was estimated by the method of spectrophotometry. The received dependences of absorbance (A) of the prepared systems from pH, varying the dose of aluminium salts after 0 and 120 minutes after preparation, are shown in Fig.1 and 2.

From Fig.1 it follows that the presence of $Al_2(SO_4)_3$ (a), $AlCl_3$ (b) and PACl (c) in model solution with a dose higher than 50 mg/l in the range of pH values of the mixed system 8.0 — 3.0 that lead to growth of A in comparison with the control solution (without a coagulant) that testifies the origin of turbidity - loss of aggregate stability, i.e. passing of coagulation process. At the decline of pH the formation of LES flocs take place. All these processes are connected with the change of surfaced charge of LES and hydration shells of dispersible particles. During the decline of pH, the values of A grow, and reach maximal values at all range of coagulant doses at pH 6.0 - 5.0 in presence of $Al_2(SO_4)_3$, pH 6.0 for $AlCl_3$ and PACl.

Lower values of A in alkaline environments are explained by increase of density of LES negative charge due to the change of dissociation degree of surfaced oxygen-containing functional groups of LES, that causes the height of forces of the electrostatic repulsion in turn.

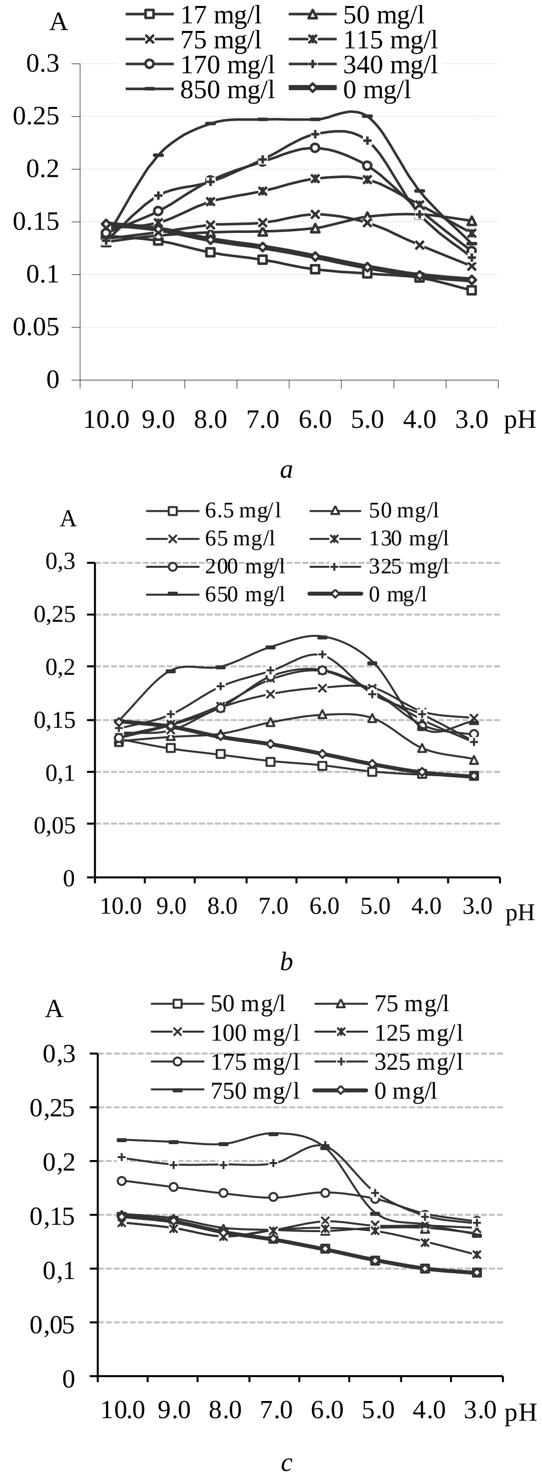
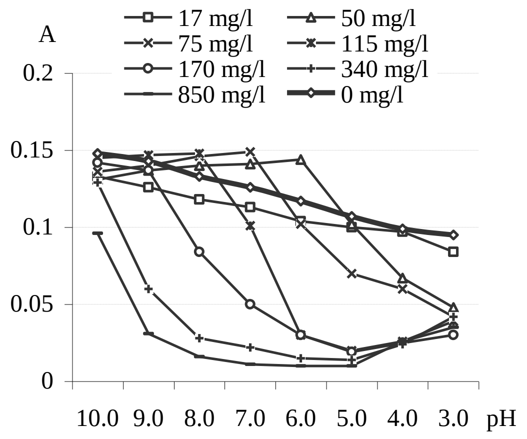


Fig.1. Dependence of absorbance on the value of the pH system and dose of $Al_2(SO_4)_3$ (a), $AlCl_3$ (b) and PACl (c) in the mixed system. Interval of time after preparation - 0 minutes

In 120 minutes there is a considerable decrease in A value, that testifies to sedimentation instability of the appearing dispersible system and is connected with settling of formed LES flakes (Fig. 2). Minimum values of A in presence of $Al_2(SO_4)_3$,

$AlCl_3$ and PACl (c) are reached at pH 5.0, 6.0 and 7.0. The largest particles of the dispersible system appear in these areas of pH.



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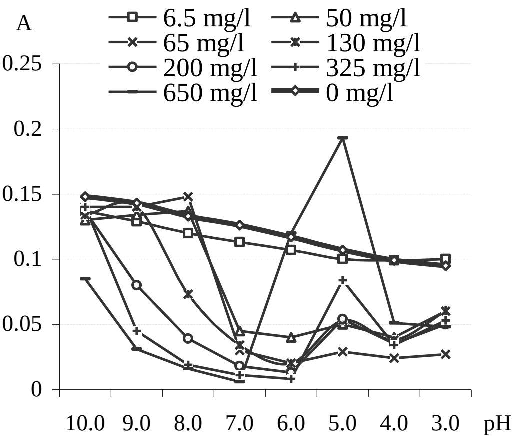

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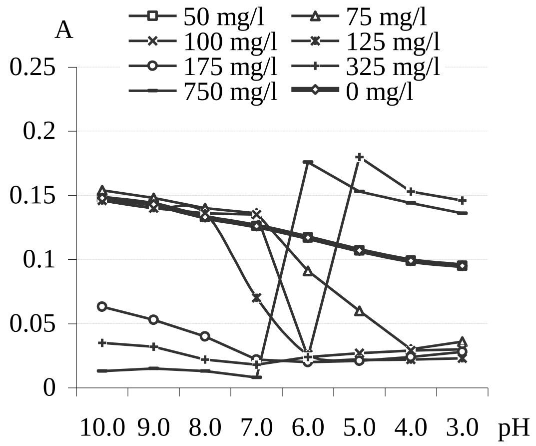

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Fig.2. Dependence of absorbance on the value of the pH system and dose of $Al_2(SO_4)_3$ (a), $AlCl_3$ (b) and PACl (c) in the mixed system. Interval of time after preparation - 120 minutes

In turn the increase of aluminium salts concentration leads to displacement of pH of educing beginning of coagulate particles of LES in the area of higher values of pH. For the process of coagulation at pH 10.0-8.0 the dose of $Al_2(SO_4)_3$, $AlCl_3$ and PACl in solution must be higher than 115, 65 and 100 mg/l, respectively. In turn it should be noted that lowering of pH to 5.0 for $AlCl_3$ with the dose higher than 130 mg/l causes the sharp worsening in the settling process of LES that leads to appearance of extremums on a Fig. 2b. It is connected with the insignificant sizes, density of appearing coagulants of LES and speed of their settling. According [2], it can be related to the recharge of LES coagulants in the interval of pH 4.0 - 5.5. Also it should be noted that appearance of extremums (Fig. 2c) in the range of pH ≤ 6.0 and doses of PACl > 175 mg/l is related to stoppage of LES settling. It is explained [5] that at the high doses of PACl in this area of pH there is a recharge of LES because of high content of hydrolysis products of PACl with a charge 4^+, and the system saves sedimentation stability. It should be noted that in presence of $Al_2(SO_4)_3$ such extreme dependences are not observed (Fig. 2a).

According [5,6,7], coagulation of LES with aluminium salts is possible to interpret as follows: the process of hydrolysis of aluminium salts, leading as far as the growth of pH to formation of the hydrolyzed forms of aluminium $AlOH^{2+}$, $Al(OH)_2^+$, begins at pH > 3.0 . It should be noted that at the hydrolysis of PACl in faintly acid environments there is a formation of dimeric structures of products of hydrolysis of $A1_2(OH)_2(H_20)_8$ with a charge 4^+ and more difficult positively charged polynuclear hydroxcomplexes, possessing high adsorption and coagulative ability in relation to negatively charged LES. At the values of pH ≥ 4.0, depending on the concentration of coagulant, formation of phase of $Al(OH)_3$, the amount of which increases, begins and the density of its charge decreases as far as approaching to the isoelectric point of $Al(OH)_3$ (pH 7.0-8.0). The further increase of pH leads to changing of charge sign of particles $Al(OH)_3$ on negative and formation of forms of $Al(OH)^{4-}$, not adsorbed on particles of LES.

A change in pH and concentration of aluminium salts can cause replacement of main mechanisms of coagulation. At low concentration of coagulant and acid values of pH, coagulation flows on the mechanism of neutralization, as a result of forming highly - charged hydrocomplexes of aluminium, at the same time during the high concentration of coagulants, LES is removed from the system in a greater degree on the mechanism of heterocoagulation of the negatively charged particles of LES with the low charged and uncharged particles of $Al(OH)_3$ [4].

As it is seen from the above mentioned data the intervals of pH of optimal selection of LES depend on the applied doses of coagulants, which is sequence of distinction of proceeding processes of particles aggregating. It is set that optimal areas of pH forming of the coagulative systems which possess high filtration features are pH 5.0 for $Al_2(SO_4)_3$, and 6.0 for $AlCl_3$ and PACl. For the optimal values of pH, the optimal doses of $Al_2(SO_4)_3$, $AlCl_3$ and PACl were found for the LES educing from model solution of hydrothermal treatment of birch wood (Fig. 3).

The efficiency of LES removal increases with the increase of coagulant dose (Fig. 3). Adding in the system $Al_2(SO_4)_3$ with a dose 75 mg/l, the efficiency is 35.71%, but increasing a dose to 115 mg/l, the value of dissolved LES removal is 81.43%. In presence of $AlCl_3$ with a dose 50 mg/l, the efficiency amounts to 61.43%, but increasing a dose to 65 mg/l, the value of LES removal is 82.86%.

In turn in presence of PACl with a dose 75 mg/l, the efficiency is 22.86%, and the increase of reagent dose to 100 mg/l is observed with sharp increase of LES educing efficiency to 79.86%.

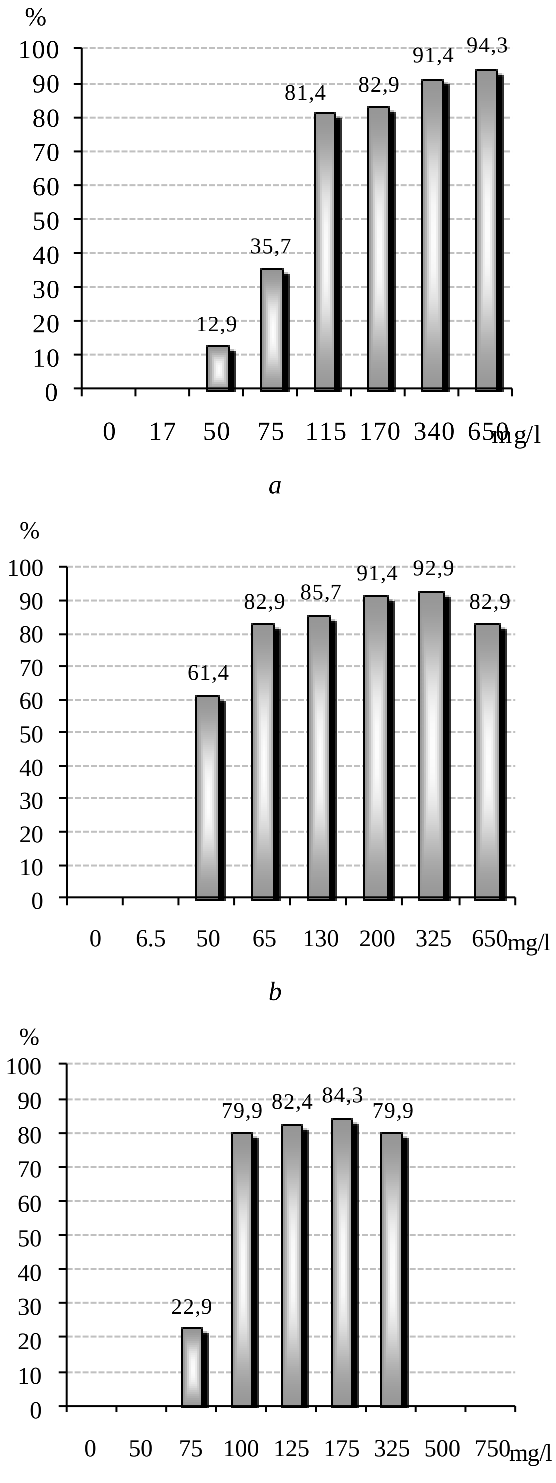

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Fig. 3. Dependence of LES removal from model solution from the dose of $Al_2(SO_4)_3$ pH 5.0 (a), $AlCl_3$ pH 6.0 (b) and PACl pH 6.0 (c)

Increase of aluminium salts doses in two and further does not result in the substantial increase of efficiency of LE educing and it is necessary to bear in mind that the increase of dose, comparatively with optimal, results not only in the overrun of coagulant and increase of remaining concentration of aluminium in the cleared wastewater but also can cause duration reduction of useful work of sedimentation tanks.

From the results showed in the Fig. 3. it follows that the optimal dose of $Al_2(SO_4)_3$ pH 5.0, $AlCl_3$ and PACl at pH 6.0 is 115, 65 and 100 mg/l, respectively.

In the Fig. 4. dependences of efficiency of model solution purification from LES are showed using $Al_2(SO_4)_3$ with a dose 115 mg/l pH 5.0, $AlCl_3$ with a dose 65 mg/l pH 6.0 and PACl with a dose 100 mg/l and pH 6.0.

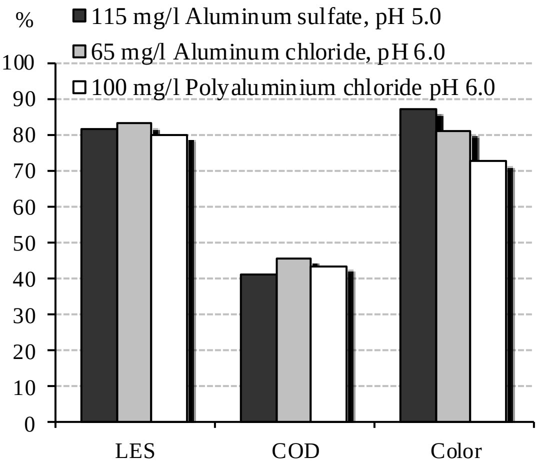

Fig.4. Efficiency of model solution purification from dissolved LES depending on the dose of $Al_2(SO_4)_3$, $AlCl_3$, PACl at the optimal values of pH and doses in the system

It is set that at the use of $Al_2(SO_4)_3$ with an optimal dose of 115 mg/l and pH 5.0 the decline of COD is 40,91%, LES educing is 81.43% and decrease of solution color was about 86.83%. An optimal dose and pH for $AlCl_3$ is 65 mg/l and 6.0, in this case the decline of COD on 45,45% is reached, LES educing is 82,86% and decrease of solution color is about 80.84%. In presence of PACl with an optimal dose of 100 mg/l and pH 6.0, the decline of COD is 43.33%, LES educing is 79.86%, and decrease of solution color is about 72.26%. The LES educing in presence of $AlCl_3$ practically takes place with identical efficiency, but at much less doses as compared to the use of $Al_2(SO_4)_3$ and PACl.

IV. Conclusions

Influence of coagulant dose and pH on the efficiency of coagulation of LES from model solutions is shown in this work. It is experimentally shown and proved:

- The critical dose of coagulation decreases at the decline of pH values;
- The increase of doses of coagulants displaces pH beginning of coagulative educing of LES in the area of higher values of pH, however maximal removal of LES from the solutions is reached in the range of pH 5.0 - 6.0;
- The optimal doses of coagulants are set: $Al_2(SO_4)_3$ – 115 mg/l, $AlCl_3$ – 65 mg/l and PACl – 100 mg/l.
- It follows from the results that an aluminium chloride at the least dose reaches larger values in LES removal and decline of COD and colour.

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Jūlija Brovkina, Galija Šuļga, Jurijs Ozoliņš. No koksnes izdalīto piesārņojošo vielu koloidālā stabilitāte alumīnija sāls klātbūtnē
Latvija ir viena no lielākajām finiera ražotājām Austrumeiropā. Viens no etapiem izejvielu sagatavošanā - bērza koksnes hidrotermiskā apstrāde. Hidrobaseinu notekūdeņiem ir augsta piesārņojuma pakāpe. Galvenie finiera ražošanas notekūdeņu piesārņojošie komponenti ir lignīns, hemiceluloze un koksnes ekstraktvielas (LES), kuras ir atbildīgas par diezgan augstu ķīmiskā skābekļa patērēšanas līmeni (ĶSP) un ūdeņu krāsu. Nepietiekami efektīva notekūdeņu attīrīšana no lielmolekulāriem komponentiem bioloģiskās attīrīšanas procesā prasa atdalīšanas koagulācijas metodes LES izstrādi un pielietojumu. Darba galvenais mērķis – noteikt LES izdalīšanās likumsakarības no modeļsistēmām atkarībā no vides pH un alumīnija sulfāta, alumīnija hlorīda un polialumīnija hlorīda devas, un noteikt LES nogulsnēšanās optimālus nosacījumus.
Modeļu šķīdumi, kurus mēs saņēmām, imitēja finiera ražošanas hidrobaseina notekūdeņus. Koagulācijas process tika veikts koagulanta un modeļu šķīduma vienādu apjomu sajaukšanas ceļā. LES izdalīšanās efektivitāti noteica pēc nostādināšanas (120 minūtes) un sistēmas filtrācijas. LES koloidālā stabilitāte alumīnija sāls klātbūtnē novērtēta ar spektrofotometrisko metodi. Filtrāta krāsa novērtēta fotometriski (ISO7887:1994). ĶSP noteikts ar oksidēšanas metodi, pievienojot kālija dihromātu (LVS ISO 6060:1989). Noteikts, ka, izmantojot $Al_2(SO_4)_3$ ar optimālu devu 115 mg/l un vides pH 5.0, ĶSP pazemināšanās sastādīja 40,91%, LES izdalīšana 81.43%, bet šķīduma krāsas samazināšanās aptuveni 86.83%. Optimāla pH un $AlCl_3$ deva ir 65 mg/l un 6.0 attiecīgi, pie tam tiek sasniegts ĶSP pazeminājums 45,45%, LES izdalīšana 82,86%, bet šķīduma krāsas samazināšana aptuveni 80.84%. PACl klātbūtnē ar optimālu devu 100 mg/l un vides pH 6.0, izraisa ĶSP pazemināšanu līdz 43.33%, LES izdalīšanu 79.86 %, bet šķīduma krāsas samazināšanu aptuveni 72.26%. LES izdalīšanās $AlCl_3$ klātbūtnē notiek praktiski ar vienādu efektivitāti, bet pie daudz mazākām devām, salīdzinot ar $Al_2(SO_4)_3$ un PACl izmantošanu. Koagulācijas metodes efektivitāte tiek regulēta ar koagulanta devu un vides pH. Šo parametru pareiza izvēle var būtiski intensificēt finieru ražošanas notekūdeņu attīrīšanas procesu, kas ir balstīts uz koagulācijas metodi.

Юлия Бровкина, Галия Шульга, Юрис Озолиньш. Коллоидальная стабильность выделяемых из древесины загрязнителей в присутствии солей алюминия
Латвия является одним из крупнейших производителей фанеры в Восточной Европе. Один из этапов в подготовке сырья – гидротермическая обработка берёзовой древесины. Сточные воды гидробассейнов характеризуются высокой степенью загрязнения. Основными загрязняющими компонентами сточных вод фанерного производства являются лигнин, гемицеллюлоза и экстрактивные вещества древесины (LES), которые ответственны за довольно высокий уровень химического потребления кислорода (ХПК) и цветность вод. Недостаточная эффективность очистки сточных вод от высокомолекулярных компонентов при биологической очистке требует применения и разработки коагуляционного метода выделения LES. Главная цель данной работы – установить общие закономерности агрегативной устойчивости LES в водных растворах в зависимости от pH и дозы сульфата алюминия, хлорида алюминия и полиалюминия хлорида, а так же определить оптимальные условия проведения процесса выделения LES из модельных систем. Процесс коагуляции производился путем смешения равных объемов коагулянта и модельного раствора. Эффективность осаждения LES при наличии солей алюминия оценивали спектрофотометрически, после двухчасового отстаивания и фильтрования системы. Методом спектрофотометрии определялась остаточная концентрация растворенных веществ в фильтрате. ХПК определялся путем окисления полученного фильтрата при внесении бихромата калия (LVS ISO 6060:1989). Цветность фильтрата определялась методом фотометрии, полученные данные соотносились с платино-кобальтовой шкалой (ISO 7887:1994). Установлено, что при использовании $Al_2(SO_4)_3$ с оптимальной дозой 115 мг/л и pH среды 5.0, снижение ХПК составило 40,91%, выделение LES 81.43%, а уменьшение цветности раствора около 86.83%. Оптимальная доза и pH для $AlCl_3$ - 65 мг/л и 6.0, соответственно, при этом достигается снижение ХПК на 45,45%, выделение LES 82,86%, а уменьшение цветности раствора около 80.84%. В присутствии PACl с оптимальной дозой 100 мг/л и pH среды 6.0, снижение ХПК составило 43.33%, выделение LES 79.86%, а уменьшение цветности раствора около 72.26%. Выделение LES в присутствии $AlCl_3$ происходит практически с одинаковой эффективностью, но при гораздо меньших дозах, по сравнению с использованием $Al_2(SO_4)_3$ и PACl. Эффективность коагуляционного метода регулируется дозой коагулянта, и pH среды. Правильный выбор этих параметров может существенно интенсифицировать процесс очистки сточных вод гидробассейнов фанерного производста, основанного на методе коагуляции.