

RIGA TECHNICAL UNIVERSITY
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**EFFICIENT SEPARATION OF BIOMASS
FROM VENEER PRODUCTION
HYDROTHERMAL TREATMENT
WASTEWATER, ITS CHARACTERIZATION
AND APPLICATION POSSIBILITY**

Summary of the Doctoral Thesis

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DOCTORAL THESIS PROPOSED TO RIGA TECHNICAL UNIVERSITY FOR THE PROMOTION TO THE SCIENTIFIC DEGREE OF DOCTOR OF ENGINEERING SCIENCES

To be granted the scientific degree of Doctor of Engineering Sciences, the present Doctoral Thesis has been submitted for the defence at the open meeting of RTU Promotion Council on 30 May 2018 at the Faculty of Materials Science and Applied Chemistry of Riga Technical University, 3/7 Paula Valdena Street, Room 272.

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DECLARATION OF ACADEMIC INTEGRITY

I hereby declare that the Doctoral Thesis submitted for the review to Riga Technical University for the promotion to the scientific degree of Doctor of Engineering Sciences is my own. I confirm that this Doctoral Thesis had not been submitted to any other university for the promotion to a scientific degree.

Sanita Vītoliņa..... (signature)

Date:

The Doctoral Thesis has been written in Latvian. It consists of Introduction; Literature review; Experimental part with evaluation of the results; Conclusions; 82 figures; 16 tables; and Reference List; the totals number of pages is 124.

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ABBREVIATIONS

| | |
|---------|---|
| A | optical density; |
| FT-IR | Fourier transform IR spectroscopy; |
| CC | composite coagulant; |
| COD | chemical oxygen demand; |
| LS | lignosulphonate; |
| MW | molecular weight; |
| MS | model solution; |
| SVI | sludge volume index; |
| WW | wastewater; |
| PAC | polyaluminium chloride; |
| PDADMAC | poly(diallyldimethylammonium chloride); |
| PEI | polyethyleneimine; |
| PEC | polyelectrolyte complex; |
| PI | permanganate index; |
| SEM | scanning electron microscopy; |
| DM | dry matter; |
| UV | ultraviolet spectroscopy. |

GENERAL CHARACTERIZATION OF THE THESIS

Topicality of the theme

One of the most important birch wood processing types with high added value in Latvia is plywood production. Currently, Latvia is one of the largest plywood producers in Eastern Europe, and its production and consumption, both in Latvia and in Europe, is increasing every year. In 2016, the quantity of the produced plywood increased by 20 % compared to 2015, reaching around 360 thousand m³ per year [1].

The topicality of the Thesis is determined by the fact that, with increasing plywood production volumes, the amount of wastewater from birch wood hydrothermal treatment basins also increases, and the plywood production technology will not be changed in the near future. Wastewater contains significant quantities of biomass – hemicelluloses, lignin compounds and extractives. These organic substances cause high chemical oxygen demand and color of the wood hydrothermal treatment wastewater. Entering natural waters, it may have a negative effect on the environment. Part of the wood processing enterprises do not have centralized wastewater treatment plants, or the applied technologies provide only the wastewater discharge to sewerage networks [2]. However, in order to gain maximum benefit, the production process should be planned as effectively as possible, striving for the development of environmentally friendly technologies, the residues of which are raw materials for another technology. It can be considered as the recovery of sustainable resources, reducing the impact on the environment, waste generation and management [3]. JSC “Latvijas Finieris” alone produces an average of 332 thousand m³ wastewater per year, which is about 730 t of wastewater biomass per year [2], [4].

It is a large enough source of renewable organic substances with the potential to obtain value added products on the basis of wastewater biomass.

Wastewater treatment by-products are basically eliminated by the combustion method for energy production [4], [5]. Those are used also in agriculture [6], creation of sorbents [7], production of construction materials [8], [9], etc. In this work, the possibility of wastewater biomass utilization in gravel road dust control is studied. Worldwide, in road dust control, calcium and magnesium chlorides are widely used, as well as soil binders on the basis of synthetic polymers, but they are relatively expensive, with low weather resistance, and some of them are not environmentally friendly [10]. When thinking about sustainable development, in Europe since 1990, more and more attention has been paid to materials of natural origin. The European Union directive [11] has already identified a number of restrictions on the use of synthetic materials, promoting the use of natural materials such as plant fibres and natural polymers. Currently, in dust control, binders based on wood chemical processing by-products, mainly technical lignin [12], which is not obtained in Latvia as a by-product, are already used. Since the wood hydrothermal treatment wastewater biomass contains large quantities of hemicellulose and lignin compounds having surface activity and binder properties as well as cation exchange capacity, this biomass has the potential for use in soil structuring.

The most common type of the removal of various suspended and colloidal pollutants from wastewater is coagulation / flocculation method. Now, aluminium and iron salts are widely used as coagulants, and cationic and anionic polymers as flocculants. However, in recent years,

studies have been focused on the creation of inorganic-organic hybrid composite systems, combining the properties of various components in one coagulant.

In accordance with the data available in the literature, inorganic-organic composite coagulants demonstrate better coagulation / flocculation efficiency compared to the traditionally used inorganic metal salt coagulants and cationic flocculants – water soluble polymers with a high molecular weight [13], [14].

Aim of the Thesis

The aim of the Thesis is to develop a new hybrid composite coagulant for biomass separation from the wastewater after wood hydrothermal treatment during veneer production, to investigate its effectiveness as a coagulant with flocculation properties, to compare it with the traditionally used cationic polymers, to characterize the formed biomass coagulate, and to evaluate the potential for the use of the obtained biomass in gravel road dust control.

The tasks of the Thesis

1. To summarize the theoretical and practical data on the used coagulants / flocculants and methods for biomass removal from wastewater in the wood processing industry.
2. To obtain a model solution in laboratory conditions, which, in terms of its chemical indicators, imitates the wastewater from hydrothermal basin of veneer production.
3. To determine and describe the composition of components of biomass of model solution.
4. To study the flocculation regularities of biomass, using the known cationic polymers as flocculants, and to determine the effect of flocculation process parameters (polymer molecular weight, dosage, pH, temperature) on the efficiency of biomass removal.
5. Based on the experimentally obtained data, to develop a new hybrid composite coagulant on the basis of the most effective cationic polymer, using for its creation the polyvalent metal salt, which is widely used in coagulation processes. To determine the effect of the hybrid coagulant's dosage, medium pH and temperature on the biomass separation yield, and the chemical composition and properties of the obtained biomass coagulate.
6. To offer a technological solution for biomass removal with the hybrid composite coagulant, which provides efficient qualitative and quantitative removal of wood biomass from wastewater.
7. To investigate the ability of the separated biomass sludge to structure dusty soil, by forming mechanically resistant aggregates, and to evaluate their potential to be used in gravel road dust control.

Main propositions put forward for defence

It is possible to develop a new composite coagulant, which is the product of interaction of polyethyleneimine and a polyvalent metal salt, and its application method, which can effectively remove the biomass, in particular low-molecular weight lignin fragments, from birch wood hydrothermal treatment wastewater.

There is a relationship between the ratios of the hybrid composite coagulant's individual components and its effectiveness under the optimum application technology.

The biomass sludge separated with the developed hybrid composite coagulant is capable of structuring dusty soil and can be used in gravel road dust control.

Scientific novelty of the Thesis

The scientific novelty of the Thesis is the development of a new hybrid composite coagulant, which is a product of interaction of a cationic polymer and a metal salt, and its technological method of use for biomass removal from the wood hydrothermal treatment wastewater. A correlation between the biomass removal efficiency and the coagulation / flocculation process parameters is investigated and established. The optimum parameters of biomass removal with the developed composite coagulant, compared with the known cationic polymers and the metal salt coagulant widely used in coagulation, are elucidated. The obtained biomass coagulants are characterized in terms of the chemical composition and properties. The advantages of the developed hybrid composite coagulant, which combines the functions of a coagulant and a flocculant, for the separation of wood hemicelluloses and lignin from wastewater are shown, compared with cationic polymers and a metal salt coagulant.

Practical significance of the Thesis

A new hybrid composite coagulant, which is a product of interaction of polyethyleneimine and a polyvalent metal salt, and the optimal application technology that enhances the efficiency of removal of biomass, especially low molecular weight lignin fragments, from wastewater and substantially reduces the coagulant's consumption, in comparison with the method when the composite coagulant's components are used as separate coagulants / flocculants, are developed.

The biomass sludge separated with the hybrid coagulant may be regarded as a value added product that can be offered as an agent in gravel road dust control.

Composition and volume of the Thesis

The Thesis is written in Latvian, it contains an introduction and 3 main chapters: Literature review, methodological part, the summary of experimental results and their evaluation, Conclusions, Reference list, 82 figures, 16 tables; in total 122 pages. The Reference list consists of 202 titles.

The work's approbation and publications

The results of the Doctoral Thesis are published in 12 scientific articles; they have been reported at 10 international scientific conferences; One LV Patent application was submitted and the approval for its publication has been received.

SUMMARY OF THE DOCTORAL THESIS

In **Introduction**, the topicality of the Thesis is justified, its goal and tasks are formulated, and the guidelines are set out.

The **first chapter** contains the literature review; more than 162 literature sources were used. It summarizes information on wastewater after wood hydrothermal treatment during veneer production and the use of coagulation / flocculation methods for wastewater biomass removal. Currently most widely used coagulants / flocculants are considered, and the choice of the composite coagulant for the removal of biomass from wood treatment wastewater is justified. Information on the current wastewater sludge application areas is gathered and, thinking about its new potential use, methods for gravel road dust control are considered. It is known that the most effective method in the wastewater purification of wood-processing industry from different suspended solids and colloidal particles is the coagulation / flocculation method. Most often, aluminium and iron salt coagulants, as well as polymer flocculants, are used as reagents.

To summarize the advantages of using polymer flocculants (significantly lower optimum dosage, greater floccules and better sedimentation kinetics, lower sludge volume, wider operating pH range, practically no effect on pH of the treated water, purified water contains no metal ions) and weaknesses (narrow optimal dosage range, mostly lower turbidity reduction efficiency, more viscous sludge) in comparison with metal salt coagulants, it can be concluded that, in order to achieve the objective of the work, polymer flocculants would be more appropriate. It is because cationic polymers with a substantial charge density have as good wastewater treatment efficiency as the traditionally used metal salt coagulants, and evaluating individual cationic polymers and their properties, PDADMAC, chitosan and PEI are chosen as the most suitable ones.

In order to increase the wastewater biomass removal efficiency and simultaneously reduce the optimum dosage of the cationic polymer, since the polymer costs are larger than the metal salt coagulants' costs, new cationic polymer-containing composite coagulant systems are investigated in the doctoral Thesis. In accordance with the literature data, the hybrid composite systems, by combining the properties of various components in one coagulant, coagulate the wastewater soluble and colloidal compounds more effectively, using the benefits of their individual components more completely.

It is rational to regard the by-products formed in the wastewater treatment process as a secondary raw material and not as a waste. From the literature data, wastewater sludge is basically eliminated by the combustion method for energy production. It is used also in agriculture, creation of sorbents, production of construction materials, etc. When thinking about the new potential use of wastewater biomass, as a result of literature analysis, the greatest practical interest is generated by the possible applications of biomass sludge in gravel road dust control. Currently, for dust control binders from the wood chemical processing by-products, mainly technical lignins, which are not obtained in Latvia as a by-product, are already used. Because the wood hydrothermal treatment wastewater biomass contains a large amount of hemicelluloses and lignin compounds having surface activity and binder properties as well as the cation exchange capacity, it has full potential for the application in soil structuring. For the development of this direction, trial experiments are necessary, on the basis of which it would be possible to establish the main regularities.

In the **second chapter**, the materials used in the study are described. The chapter describes the experimental course of the work, and the used methods for analysis and testing (Fig. 1).

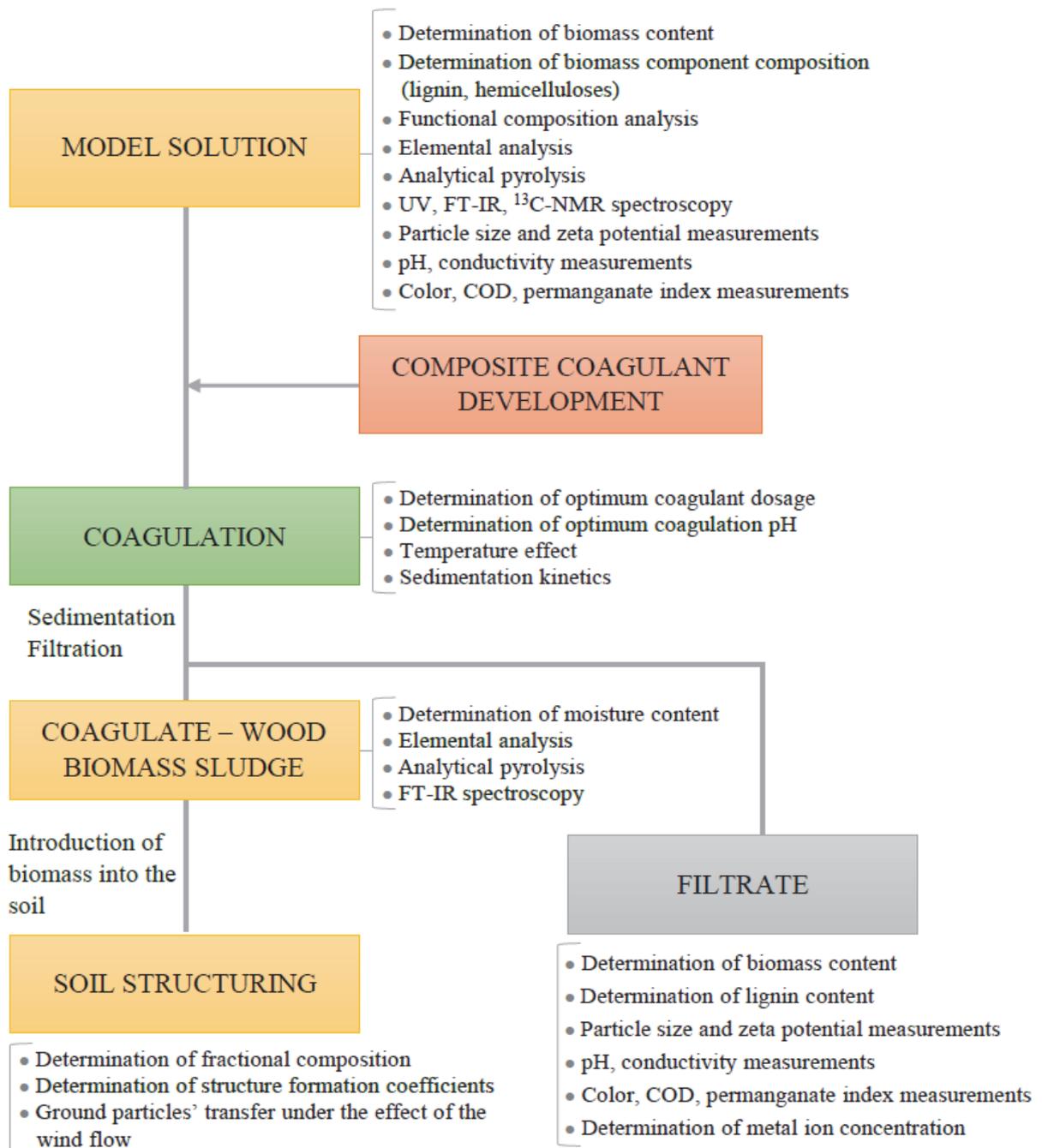


Fig. 1. Experimental course of the work, methods used for analysis and testing.

The **third chapter** is devoted to the summary and evaluation of the experimental results.

RESULTS OF THE THESIS AND THEIR EVALUATION

Characterization of the model solution and its biomass

Taking into account the fact that the composition of the birch wood pre-treatment wastewater used in veneer production is inconstant, investigation of the coagulation mechanism and the effect of it or other factors on the hydrothermal basin wastewater treatment requires a model system with unambiguous, stable characteristics. Model solution (MS) obtained in laboratory conditions, which imitates real wastewater after wood hydrothermal treatment process during veneer production, is used for the studies. The characterization parameters of the obtained MS are shown in Table 1.

Table 1

Parameters of Model Solution

| pH | Biomass content, mg/l | Density, g/cm ³ | COD, mgO/l | PI, mgO/l | Color, mg/lPt |
|---------|-----------------------|----------------------------|------------|-----------|---------------|
| 9.0–9.1 | 1400±67 | 0.998 | 1285±30 | 320±10 | 746±19 |

The amount of MS biomass is 1400±67 mg/l, 7.1 % of the initial particle mass. The obtained MS is a medium alkalinity solution with average chemical oxygen demand (COD) and permanganate index (PI) values. The high color indicates the presence of lignin and its derivatives.

So that the MS would correspond to the real production wastewater, for comparison purposes, wastewater samples from wood hydrothermal processing basins of a plywood production enterprise are taken. The chemical analysis of MS and wastewater (WW) biomass shows that their compositions are very similar (Table 2).

Table 2

Elemental and Functional Composition of the Model Solution and Wastewater Biomass

| Sample | C % | H % | O % | N % | S % | Inorg. subst. % | OCH ₃ % | CO % | OH % |
|--------|-------|------|-------|------|------|-----------------|--------------------|------|-------|
| WW | 42.13 | 5.35 | 51.10 | 0.64 | 0.31 | 0.47 | 1.86 | 1.05 | 9.25 |
| MS | 37.75 | 4.78 | 56.69 | 0.30 | 0.14 | 0.34 | 2.29 | 1.50 | 10.15 |

The results obtained by the chemical analysis of MS and WW biomass samples are corroborated by the registered FT-IR and UV spectra (Figs. 2 and 3).

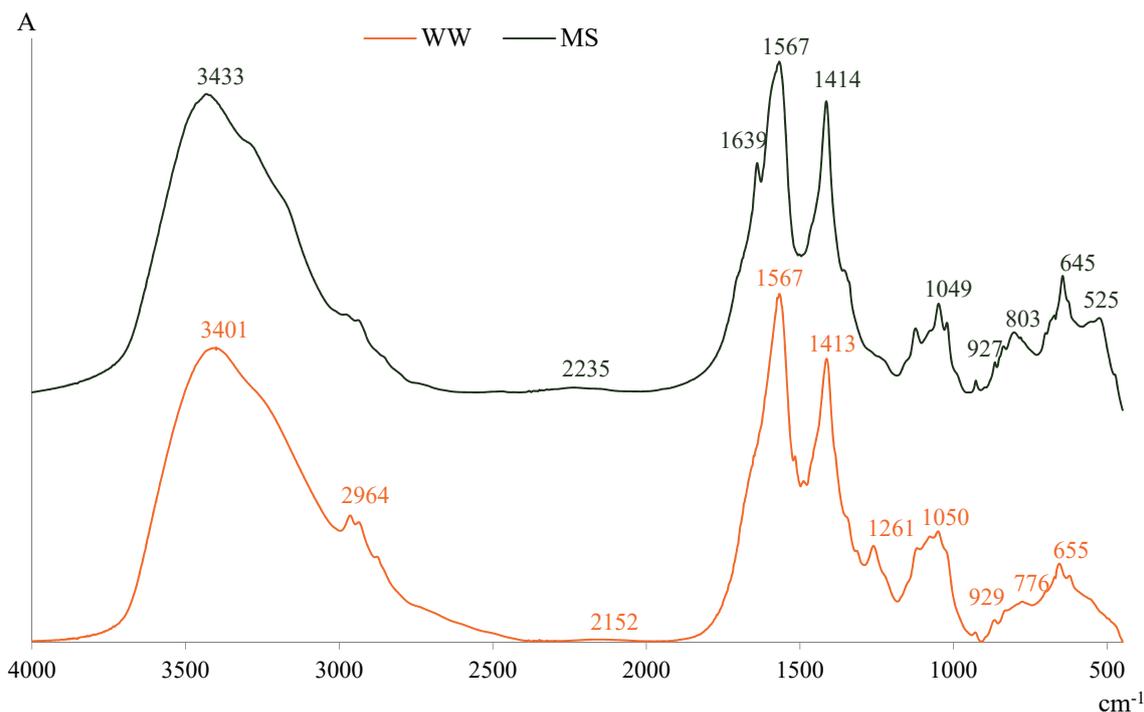


Fig. 2. Spectra of WW and FT-IR of MS biomass samples.

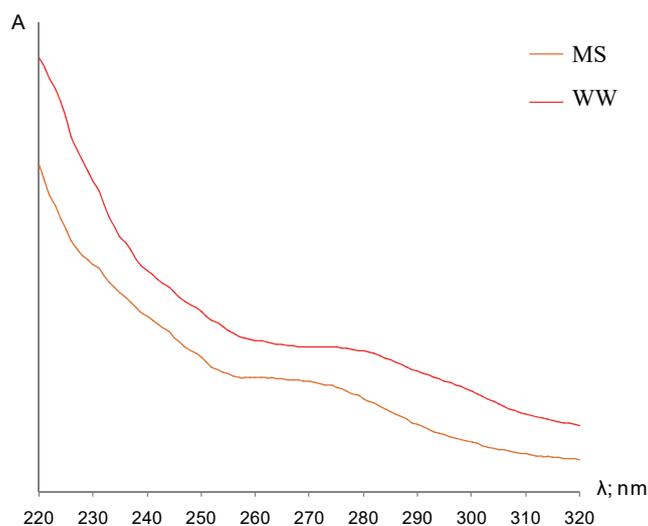


Fig. 3. UV spectra of WW and MS samples, pH 7.5.

At the same time, also the changes of component composition of birch chips in the hydrolysis process were considered. In accordance with the obtained results shown in Fig. 4, the hydrolysis process has the most significant impact on the cellulose and hemicelluloses content. The content of cellulose increases by 6.5 % and that of hemicelluloses decreases by 5.6 %, while the lignin content decreases by only 0.1 %. There is a reason to believe that the substantial increase in the cellulose content and the minimum changes in the lignin content are connected with the significant loss of hemicelluloses and water-soluble extractives as a result of hydrolysis of birch wood chips.

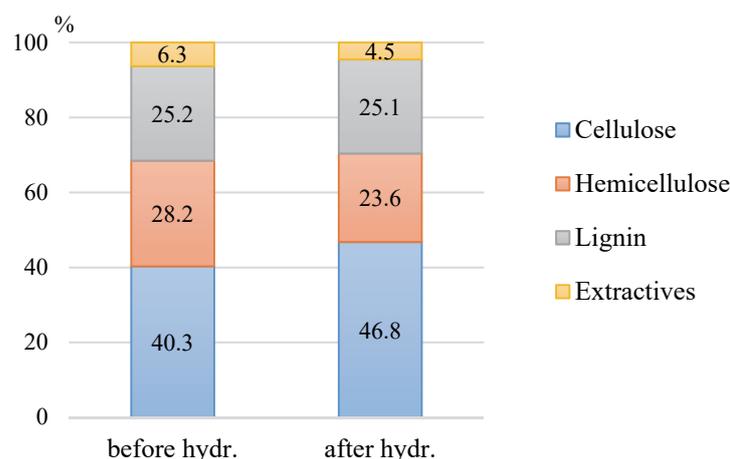


Fig. 4. Component composition of birch wood chips before and after hydrolysis.

Biomass fractionation was carried out in accordance with the methodology. The obtained results show that the biomass contains 13.5 % of lignin and 75.2 % of hemicellulose fractions. At the same time, the products of destruction of the low MW lignocellulosic matrix, which cannot be separated by this method, make up 11.3 %. The ratio of lignin, hemicelluloses and water-soluble wood destruction products is 1.2/6.7/1.0.

Biomass removal with cationic polymers

Using cationic polyelectrolytes (Table 3) with different molecular weight, the efficiency of biomass removal from the birch wood hydrothermal treatment model wastewater was studied to select the most efficient cationic polymer for the development of a new composite coagulant.

Table 3

Cationic Polyelectrolytes Used in Experiments

| Polymer | Molecular weight | Characteristics |
|---|------------------|---|
| Poly(diallyldimethyl ammonium chloride) (PDADMAC) | 100 000–200 000 | 20 % water solution |
| | 200 000–350 000 | 20 % water solution |
| | 400 000–500 000 | 20 % water solution |
| Chitosan | 200 000 | powder-like, deacetylation degree 75–85 % |
| | 350 000 | powder-like, deacetylation degree 75–85 % |
| | 500 000 | powder-like, deacetylation degree > 75 % |
| Polyethyleneimine (PEI) | 1 300 | 50 % water solution |
| | 750 000 | 50 % water solution |

It is known that water-soluble low-molecular weight lignins and hemicelluloses with cationic polymers in the water medium mainly interact in accordance with the electrostatic mechanism [15]. As a result of the electrostatic interaction between the polymer and the biomass components, polyelectrolyte complexes (PEC) are formed.

In the flocculation process, when determining the flocculant's efficiency, a significant role is given to its dosage and pH. The flocculant's optimum dosage is determined by the total biomass removal efficiency, as well as by the amount of removed lignin and the decrease of the MS permanganate index (PI).

Table 4 gives a comparison of the efficiency of the used cationic polymers at the optimum flocculation parameters. The total biomass removal efficiency for all polymers is similar, reaching 91–93 %. Significant differences are observed in the lignin extraction efficiency. For chitosan it is by about 16–18 % lower than for PDADMAC and PEI, which directly correlates with the MS color reduction.

An important flocculation parameter is pH. Using PEI, as compared to PDADMAC, in the flocculation process it is not necessary to use alkali to ensure the desired pH; also pH fits in the permissible pH value range for wastewater prior to its discharge to the sewerage network or for reuse. The optimum pH for PEI corresponds to the optimum pH range (5–7) of metal salt coagulants, which is important in the creation of composite coagulant systems with metal salts.

Table 4

| Parameters | PDADMAC | Chitosan | PEI |
|----------------------|-------------|----------|----------|
| MW | 100–200 KDa | 350 KDa | 750 KDa |
| Optimum dosage, mg/l | 50 | 35 | 35 |
| Optimum pH | 7–8 | 5 | 6 |
| Biomass, mg | 1288±12 | 1285±6 | 1309±4 |
| Lignin, mg | 171±7 | 126±2 | 175±2 |
| Color removal, % | 88.6±1.5 | 85.2±0.8 | 91.4±1.2 |
| COD removal, % | 39.2±2.4 | 41.9±1.7 | 44.0±1.8 |

The advantages of the technological method for MS biomass removal with PEI are as follows:

- relatively small optimum dosage (25–35 mg/l);
- optimum flocculation pH 6. The flocculation process does not need the use of pH regulators to ensure the required pH, and pH fits in the wastewater permissible pH value range prior to its discharge to the sewer or for reuse. Compatibility of pH with metal salts coagulants' optimum pH range;
- good sedimentation kinetics.

Biomass removal with composite coagulant

Based on the results obtained, PEI with a high molecular weight (750 KDa), which showed the best flocculation ability, is selected as the composite coagulant (CC) component together with the polyvalent metal salt, which is widely used in wastewater treatment. Owing to the hybrid nature, since it consists of an organic flocculant and an inorganic coagulant, the obtained

composite coagulant simultaneously performs both the coagulation and flocculation function. This allows to raise the biomass removal efficiency and simultaneously reduce the optimum PEI dosage, because the polymer costs are higher than the costs of polyvalent metal salts. In the composite coagulant, a smaller metal salt dosage is required in comparison with the case of a pure metal salt coagulant, which will allow reducing the residual metal ion content in the treated water and the risk to the environment.

The composite coagulant in the polymer colloidal complex form, containing PEI and polyvalent metal ions, is formed due to the donor-acceptor interaction between the uncharged nitrogen atoms in imine groups and metal ions (Fig. 5). Taking into account the hydration shell around the metal ions, the complex is stabilized with hydrogen bonds. Such a kind of hybrid coagulants has to possess a greater coagulation and flocculation ability, because it consists of a high-molecular weight polymer, which is characterized by a high flocculation ability, and a hydrolyzed metal salt, which possesses a pronounced coagulation function.

The coagulation / flocculation process for the biomass removal from the model solution with the developed CC can be described as the adsorption of hemicelluloses and lignin fragments on the CC particle surface as a result of the neutralization of biomass surface polar groups ($-OH$ and $-COOH$) and CC positively charged surface amino groups, followed by the aggregation of biomass coagulated particles, owing to the “bridge formation” mechanism.

To evaluate the coagulation efficiency of the developed composite coagulant, as the reference coagulation – the control, the previously developed metal salt composite coagulant on the polyaluminium chloride (PAC) base [16], which exhibits improved wood processing wastewater coagulation effectiveness compared with PAC, is selected.

In this study, the PEI/metal salt mass ratio in the composite coagulant varies in the range of 0.16–1 or the PEI content of 14–50 %. The highest yield of biomass and lignin removal, 1364 mg/l and 194–201 mg/l, respectively, is reached at the 25–35 % PEI content in the composite coagulant (Fig. 6).

From the obtained results, two optimum compositions are selected for the composite coagulant: CC-25 (25 % PEI) and CC-35 (35 % PEI), which exhibit the best coagulation efficiency for the biocomposite.

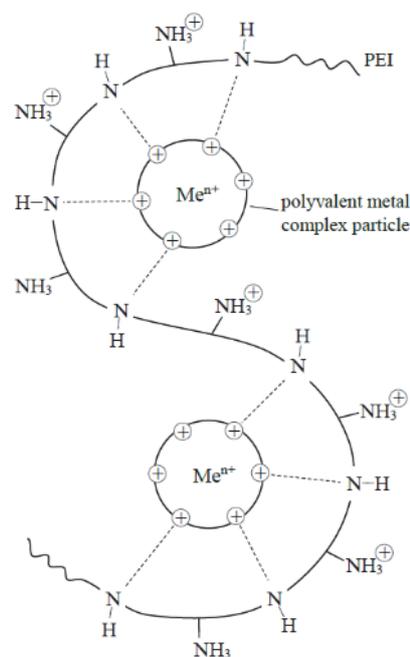


Fig. 5. Structure of composite coagulant.

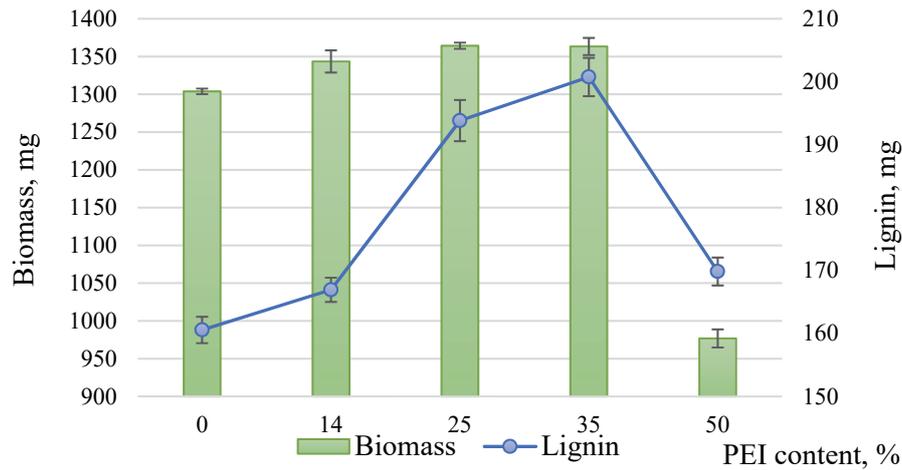


Fig. 6. Total removal efficiency of biomass and lignin depending on the PEI content in the composite coagulant, pH 6.

Figure 7 shows the average particle diameter and zeta potential of CC-35, PEI of its components and metal salt. Compared with the case of the metal salt and PEI, the particles of the obtained composite coagulant CC-35 are characterized by a higher zeta potential and a greater average particle diameter, which indicates the formation of new coagulant particles as a result of the interaction of PEI and polyvalent metal ions.

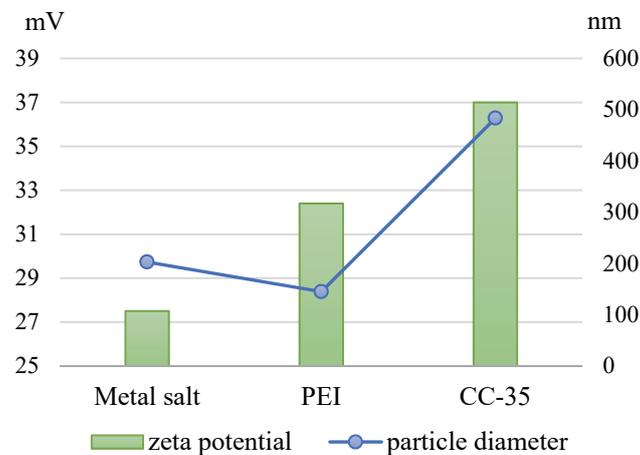


Fig. 7. Zeta potential and average particle diameter for the composite coagulant CC-35 and its components, pH 6.

The interaction of PEI and the polyvalent metal salt in the composite coagulant is also testified by the UV spectra (Fig. 8).

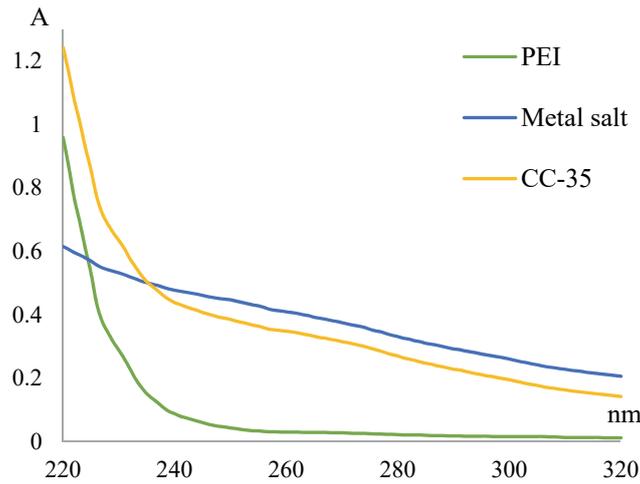


Fig. 8. UV-spectra of the composite coagulant CC-35 and its components.

The efficiency of CC-25 and CC-35 biomass and lignin removal is studied by varying the coagulant dosage at pH 6 (PEI optimum flocculation pH). Figure 9 shows that by increasing the composite coagulant dosage from 40 to 70 mg/l, the biomass yield also increases, reaching 1353–1358 mg/l, or 97 %. The effect of further increasing of dosage on the amount of the removed biomass quantity is no longer so pronounced, and already at a dosage >100 mg/l the coagulant efficiency decreases. In the case of lignin, the removal efficiency increases linearly with the coagulant dosage’s increase even up to 100 mg/l with CC–35, and 120 mg/l with CC–25, reaching a 201–203 mg/l lignin yield, or 65 %.

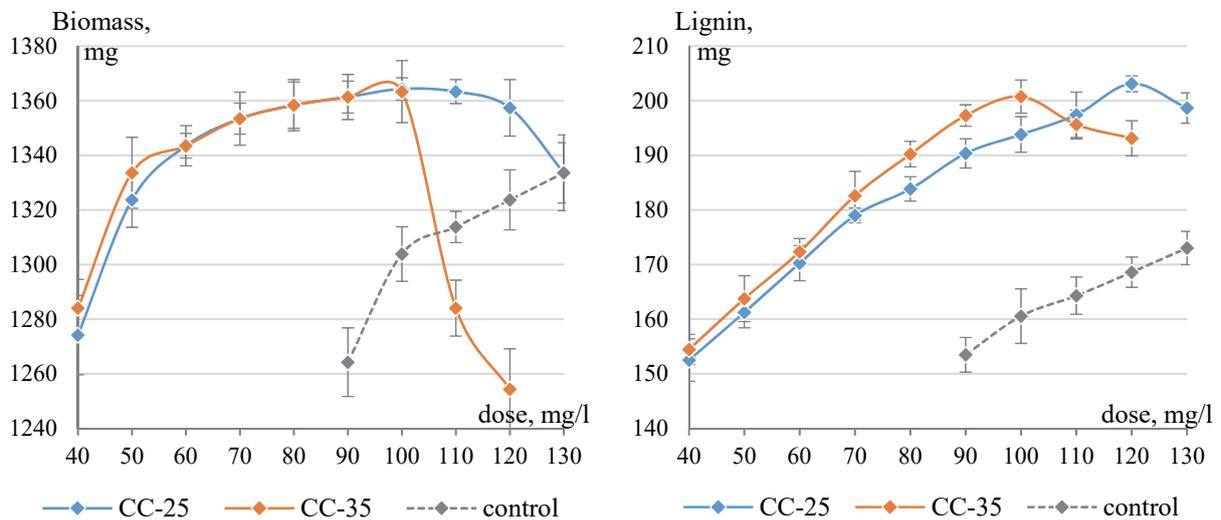


Fig. 9. Total biomass and lignin removal efficiency depending on the coagulant dosage, pH 6.

The coagulant’s optimum dosage for biomass removal can be estimated by the changes in the MS zeta potential after its treatment. Increasing the CC-25 and CC-35 dosage up to 70 mg/l, the biomass removal increases, which is testified by the zeta potential values approaching 0 (Fig. 10). It can be seen that the zeta potential changes correlate very well with the composite coagulant dosage. Between the filtrate zeta potential and the CC-25 and CC-35 dosage, there is

a linear correlation ($R > 0.97$), which confirms the coagulation charge neutralization mechanism, according to which the optimum yield of biomass is reached when the zeta potential is close to 0. The negative values of the filtrate zeta potential exceed 0 at the CC-25 and CC-35 dosages > 70 – 80 mg/l. With further increase of the coagulant dosage, zeta potential for the filtrate becomes positive, which points to the composite coagulant dosage superiority. In turn, for the control coagulant, the optimum dosage exceeds 130 mg/l, because at this dosage, the filtrate zeta potential still remains negative, which indicates that the complete neutralization of biomass particles has not yet occurred.

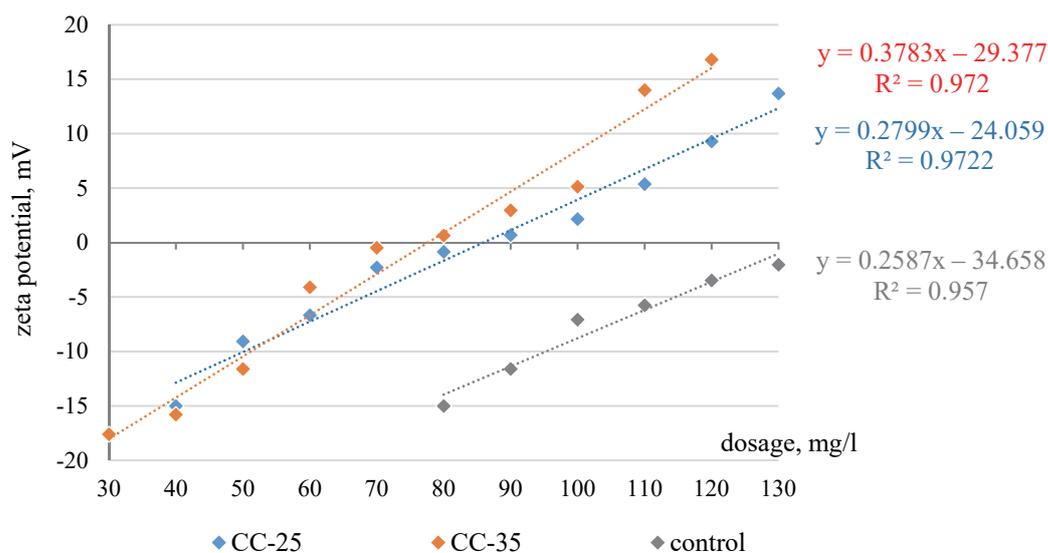


Fig. 10. Zeta potential of the model solution after coagulation and filtration, depending on the coagulant dosage, pH 6.

The coagulation / flocculation ability of the composite coagulant in the pH range of 5–8 was studied. Fig. 11 shows that the amount of the separated biomass increases by increasing the pH from 5 to 6 and further decreases in neutral and alkaline media. The composite coagulant demonstrated the best lignin extraction efficiency at pH 6–7. It can be concluded that the optimum pH with the composite coagulant, as well as with PEI, is pH 6.

Since the coagulation / flocculation process is relatively sensitive to temperature changes, the efficiency of the composite coagulant in the temperature range of 13–60 °C was compared. Throughout the investigated temperature range, the maximum biomass yield is at pH 6, and the coagulation / flocculation efficiency decreases with the pH increase. The decrease of temperature below 20 °C practically does not affect the composite coagulant biomass yield at the optimum pH 6, but at pH > 6 deterioration of the efficiency of coagulation / flocculation due to the increase in the MS dynamic viscosity is observed.

At the same time, raising the temperature up to 40 and 60 °C, the composite coagulant's efficiency decreases, which is explained by the decrease in the lignin molecules' dissociation degree at elevated temperatures. The best lignin yield is at 13 °C, which is connected with the fact that at lower temperatures the contribution of hydrogen bond formation into the biomass deposition increases.

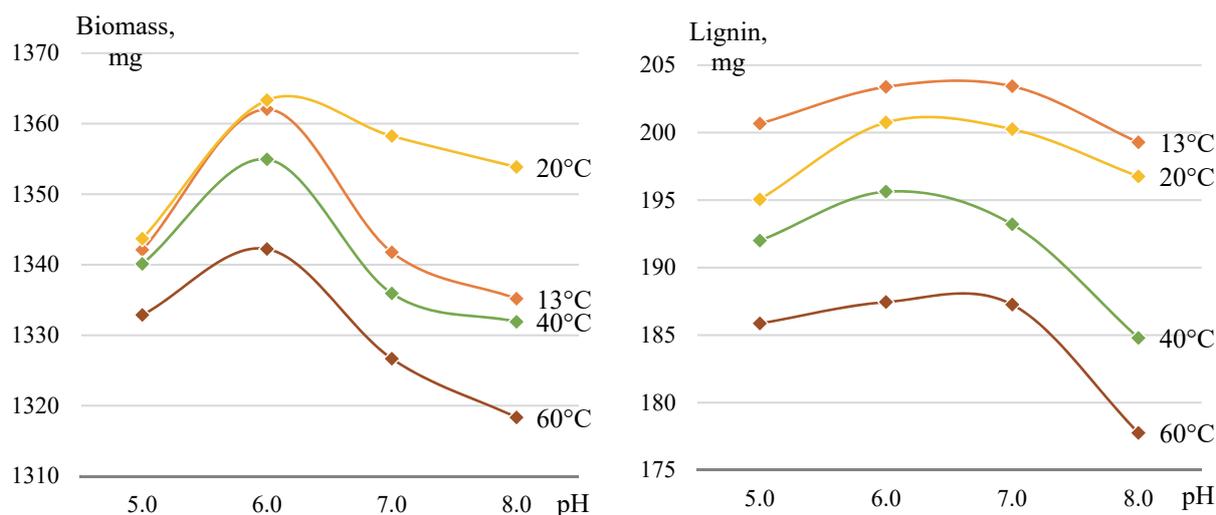


Fig. 11. Total biomass and lignin removal efficiency depending on the pH and temperature, CC-35 dosage 100 mg/l.

Fig. 12 shows that the coagulation / flocculation process with the composite coagulant has the highest initial turbidity as compared with the MS treated with PEI and the control coagulant. As demonstrated by the analysis of the sizes of the floccules formed, the diameter of the floccules obtained with CC-35 after 30 min coagulation / flocculation varied in the range of 1114–1242 nm; at the same time, the sizes of the floccules formed with the PEI and control coagulant were significantly lower, i.e. 664–842 nm and 331–499 nm, respectively.

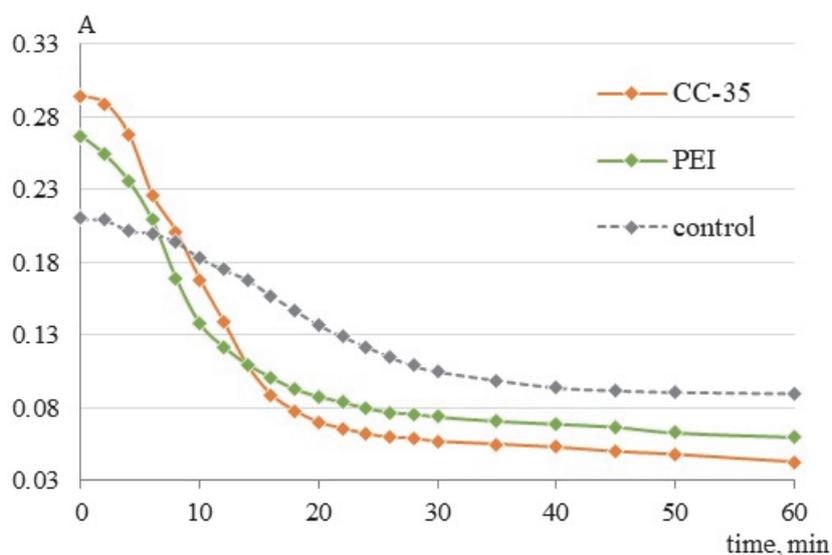


Fig. 12. MS absorbance (490 nm) in the coagulation / flocculation process, depending on time, the dosage 70 mg/l, pH 6.

Table 5 shows a comparison of the optimum parameters (dosage, pH) and efficiency (biomass and lignin yield, the color of treated MS, COD, etc.) of the coagulation / flocculation of the control coagulant and the composite coagulants CC-25 and CC-35.

Table 5

Efficiency of Coagulants / Flocculants at Optimum Parameters

| Parameter | PEI | control | CC-25 | CC-35 |
|----------------------|----------|------------|------------|------------|
| Optimum dosage, mg/l | 35 | 100 | 80 | 70 |
| Optimum pH | 6 | 6 | 6 | 6 |
| Biomass, mg | 1309±4 | 1304±11 | 1358±8 | 1353±6 |
| Lignin, mg | 175±2 | 161±5 | 184±2 | 183±5 |
| Color removal, % | 91.4±1.2 | 85.4±0.8 | 89.8±0.7 | 89.3±1.1 |
| COD removal, % | 44.0±1.8 | 46.7±2.1 | 49.7±1.6 | 47.8±2.0 |
| Metal ions, mg/l | – | 0.063±0.03 | 0.032±0.02 | 0.025±0.02 |
| SVI, ml/g | 42±11 | 107±4 | 74±6 | 74±4 |

It can be seen from the obtained results that using CC-25 and CC-35 it is possible to achieve a greater yield of biomass. The total biomass removal efficiency increases from 93 % to 97 % compared with the PEI and control coagulant.

In order to achieve a greater biomass removal efficiency using a PEI mixture with a polyvalent metal salt as a coagulant, a lower PEI amount is necessary. The effective dosage of the composite coagulant PEI is by 30–43 % lower than that in when using only PEI, but the metal salt dosage in the composite coagulant is by 40–55 % lower than the optimum control coagulant dosage, which allows a significant reduction in the concentration of the metal ions remaining in the solution. An analysis of the obtained results has shown that the concentration of residual metal ions in MS after treatment with the composite coagulant is 2–2.5 times lower than that after the treatment with the control coagulant.

In accordance with the obtained results, CC-25 and CC-35 are characterized also by a good sedimentation kinetics, which is confirmed by the sludge volume index values. It can be seen that for CC-25 and CC-35 this index is lower than 100 ml/g, which is an important parameter from the technological point of view.

It is known that when adding a polyvalent metal salt coagulant, pH of the treated water decreases, and its decrease depends on the initial pH value of the wastewater. In this study, the effect of the control coagulant on pH of the investigated model solution is regarded. As demonstrated by the obtained results, by adding the optimum control coagulant dosage, pH in the model solution decreases to pH 4. In order to achieve the control coagulant's optimum pH value 6, in the coagulation process, sodium hydroxide (NaOH) should be added to the model solution. In turn, by using the composite coagulants CC-25 and CC-35, the pH values of MS varied in the range of 6.0–6.5, which already is the optimum coagulation pH, and it is not necessary to add NaOH to achieve the required pH, which is a substantial advantage from the reagent-saving and cost viewpoint.

It is concluded that the composite coagulant properties and the biomass coagulation / flocculation efficiency may vary, changing the PEI and metal salt ratio in a narrow range. In the laboratory model system, the best coagulation / flocculation efficiency is demonstrated by

the composite coagulant with the 25–35 % of PEI and 75–65 % of metal salt content at the optimum dosage of 70–80 mg/l, reaching 1353–1358 mg/l, or 97 % of the total biomass yield and 184 mg/l, or 60 % of the lignin yield.

Characterization of biomass sludge

In the wastewater coagulation / flocculation process, sludge – coagulate – is formed. Biomass sludge is difficult to dewater, because already at low concentrations, it forms a network gel with water. The sludge, which is isolated from MS with the composite coagulant CC-35 (dosage 70 mg/l, pH 6.0), is characterized by high moisture content of 98.7 %, which is 93 % after centrifugation.

Table 6 lists the elemental composition of the obtained biomass sludge.

Table 6

Elemental Composition of the Obtained Biomass Sludge

| C | H | O | N | Me | anions |
|------|-----|------|-----|-----|--------|
| % | % | % | % | % | % |
| 32.9 | 4.7 | 54.3 | 4.2 | 2.7 | 0.8 |

Figure 13 shows the biomass sludge – coagulate that is formed in the coagulation / flocculation process with the composite coagulant and part of the uncoagulated biomass.

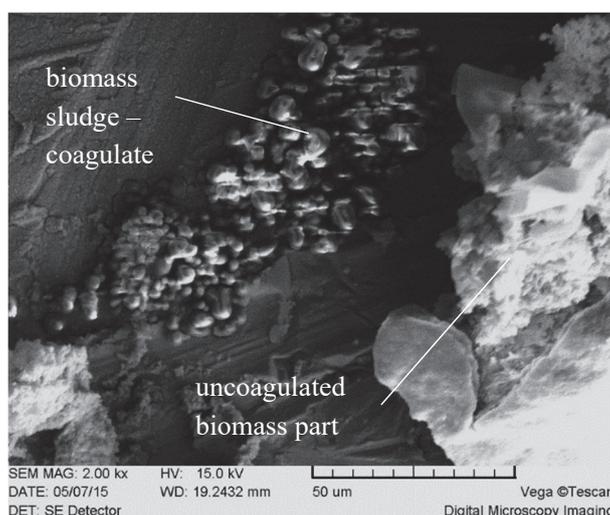


Fig. 13. Microphotograph of coagulated and uncoagulated biomass.

Use of biomass sludge in soil structuring

Since the biomass coagulate surface contains both completely hydrophobic regions, which are formed as a result of the interaction of biomass components with CC, and free functional groups (carboxyl-, hydroxyl-, amino-), which are located in the coagulate fault segments (e.g., tails, loops), biomass coagulates exhibit binding properties.

Hence, the work studies the ability of the biomass separated from wastewater to structure powder-like soil and form mechanically resistant aggregates with the potential use in gravel road dust control. The biomass is used in a wet state (moisture content is 93 % on the average) after centrifugation, without its drying. The biomass suspension with a defined concentration is obtained by diluting the biomass with water and actively mixing.

The wastewater biomass particle adsorption in the sand soil can occur under the effect of Van der Waals forces or as a result of the formation of hydrogen bonds between the sand Si-OH and the biomass particles' carboxyl-, hydroxyl- and amino groups, which are located in the coagulate fault segments. With the clay content's increase in the soil composition, besides the hydrogen bonds formation and the effect of Van der Waals forces, the contribution of the hydrophobic interaction between the biomass and the soil particles increases.

An important parameter that shows the effectiveness of the structure forming agent is the aggregate composition of the treated soil. The fractional composition of the sand soil treated with the biomass suspension is shown in Fig. 14. The treated sand soil samples primarily contain the medium-sized fraction with a diameter of 1–3 mm. With increasing biomass content in the soil, also the amount and sizes of sand aggregates increase. It is testified by the increasing values of the structure formation coefficient K_1 , which indicates the total structuring ability, and K_2 , which shows the ability to form aggregates with a diameter greater than or equal to 3 mm (Fig. 15). Increasing the biomass content in the soil from 0.6 % to 0.8 %, a rapid improvement of the biomass structuring efficiency occurs. The soil sample's structured part increases from 10 % to 50 %. The amount of average fractions with a diameter of 1–3 mm significantly increases, and the formation of aggregates with a diameter > 3 mm significantly improves.

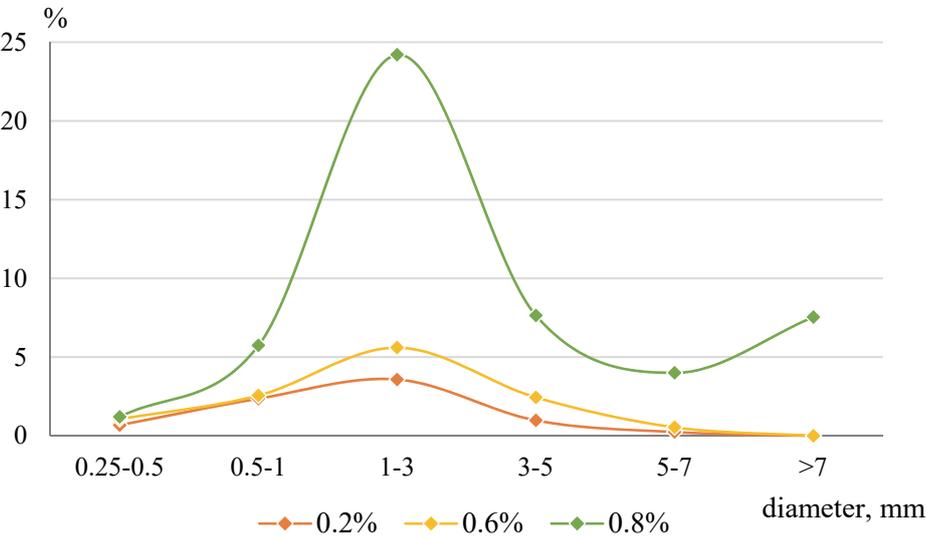


Fig. 14. Fractional composition of the treated sand soil depending on the content of biomass sludge in the soil (100 % sand soil).

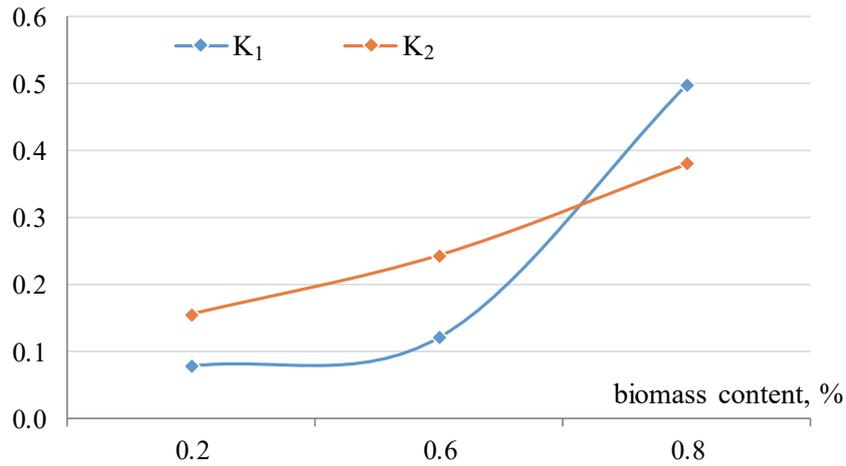


Fig. 15. Structure formation coefficients K_1 and K_2 depending on the biomass sludge content in sand soil (100 % sand soil).

As the gravel road surface is formed not only of sand, also a sand / clay model soil with the clay content of 0–70 % is used in the studies. The obtained results show that the increase of the clay content in the soil improves the soil aggregate composition (Fig. 16). Using the 0.8 % biomass in sand soil, the total aggregate mass is 50 % of the soil mass; in turn, using a model soil with a 30 % clay content, the amount of aggregates rapidly grows and represents 91 % of the soil mass (Fig. 17, K_1). Compared with the pure sand soil, on the whole, the amount of fine fractions in soil decreases and the proportion of coarse fractions increases, which is clearly confirmed by the coefficient K_2 values (Fig. 17).

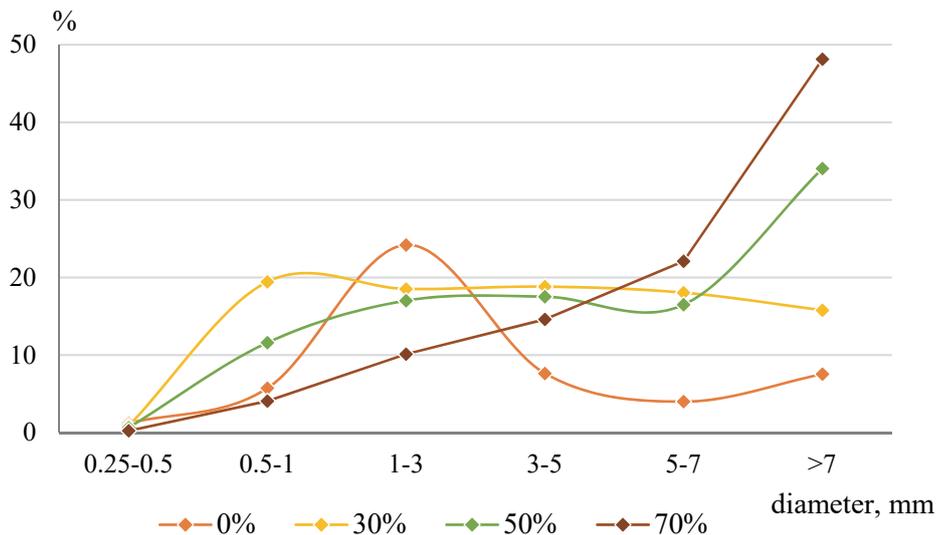


Fig. 16. Fractional composition of the treated model soil depending on the clay content in the soil (0.8 % of biomass).

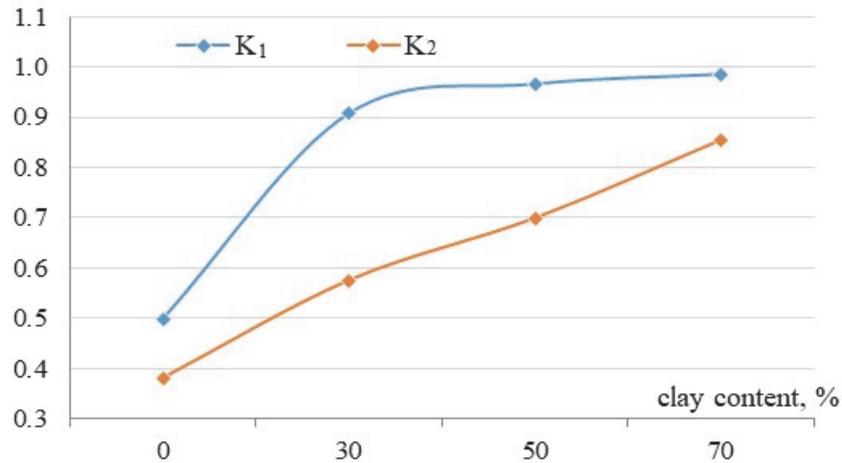


Fig. 17. Structure formation coefficients K_1 and K_2 depending on the clay content in the soil (0.8 % of biomass).

For assessment of the wastewater biomass soil structure formation capacity, as a comparative reagent lignosulphonate (LS), now already widely used in gravel road processing, which is a wood chemical processing by-product, is selected. When treating the sand soil with the separated biomass, the total aggregate mass is 50 % of the soil mass, while using the LS, the amount of aggregates is higher and accounts for 70 % of the soil mass (Fig. 19, K_1). At the same time, the separated biomass is capable of forming aggregates of a larger diameter than LS, which is testified by the coefficient K_2 values (Fig. 19). Figure 18 shows that the soil samples structured with LS are primarily composed of the fraction with a diameter of 0.5–1 mm (32 %), but the samples structured with the separated biomass contain mainly the larger size fraction with a diameter of 1–3 mm (24 %). It can be concluded that the soil structured with the biomass is characterized by better resistance to wind erosion, which is essential in the dedusting process.

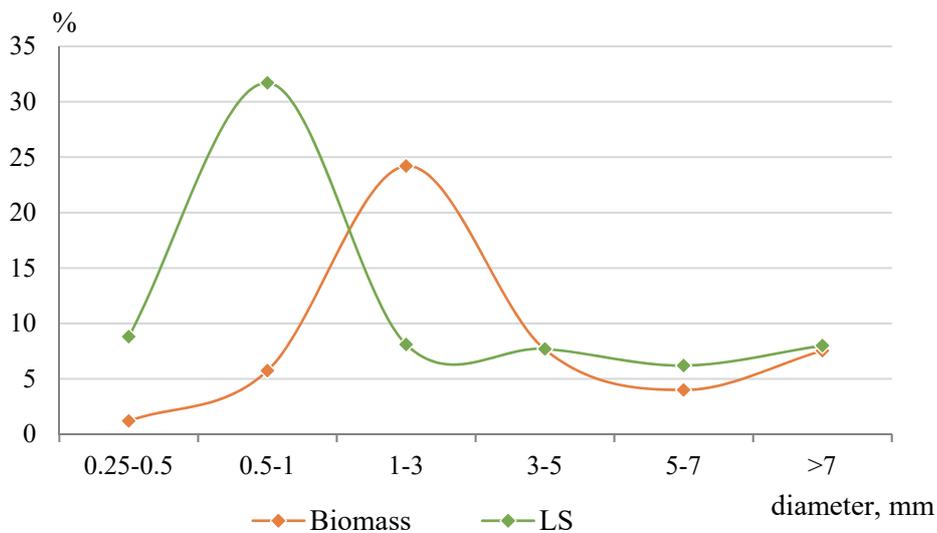


Fig. 18. Fractional composition of the sand soil treated with the separated biomass and lignosulphonate, concentration – 0.8 %.

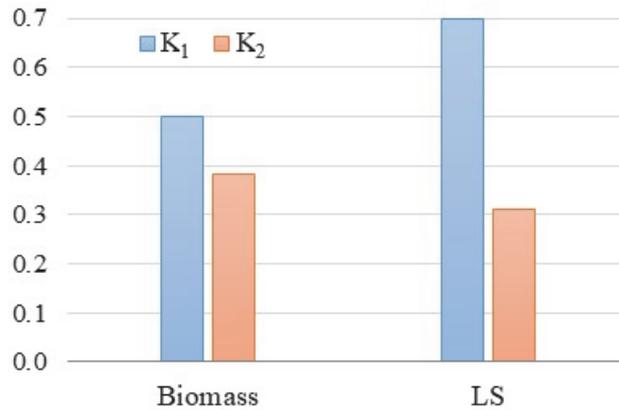


Fig. 19. Structure formation coefficients K_1 and K_2 of the sand soil treated with the separated biomass and lignosulphonate, concentration – 0.8%.

As a result of the impact of wind, the gravel road surface dust is subjected to active transfer. The critical speed of wind at which the particle movement starts, depends on the soil particle sizes. The movement of soil particles under the influence of wind flow depending on the particle size is seen in Fig. 20.

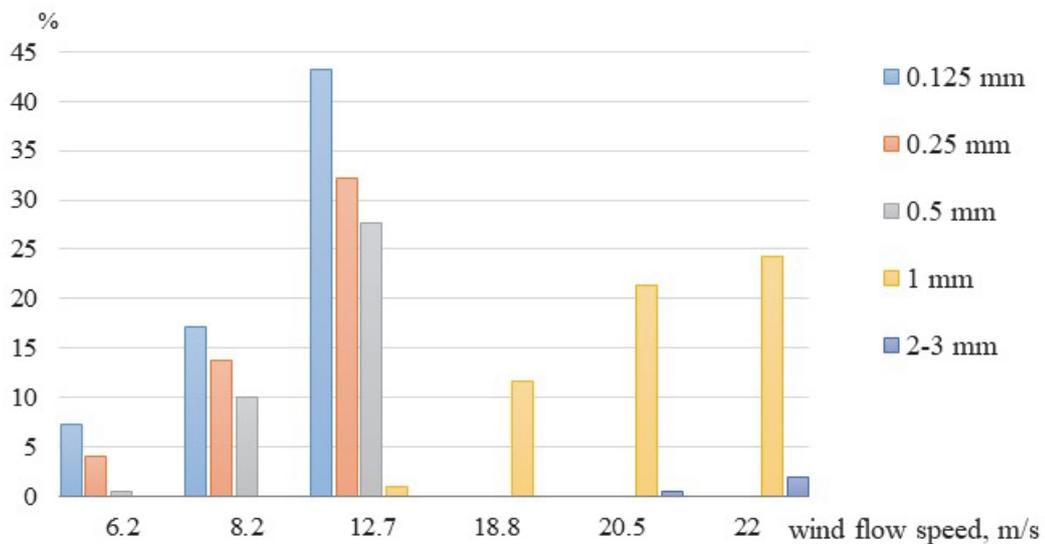


Fig. 20. Movement of soil particles under the influence of wind flow depending on the particle size.

It can be seen that the movement of soil particles with a diameter < 0.5 mm begins at a wind flow speed of 6 m/s. The smaller the particle diameter, the greater is the mass of eroded soil particles. For particles with a diameter of 1 mm the wind flow speed at which particles start to move is 12 m/s, and when the flow speed is increased up to 22 m/s, the mass of eroded particles does not exceed 24 %. As can be seen, particles with a diameter > 2 mm are the most resistant against wind erosion. Their movement starts only at a wind flow speed of 20 m/s and at a wind speed of 22 m/s the mass of eroded particles does not exceed 2 %.

Technological scheme of biomass separation and use

Figure 21 shows a variant of the technological scheme of separation and use of veneer production wood hydrothermal treatment basin wastewater biomass.

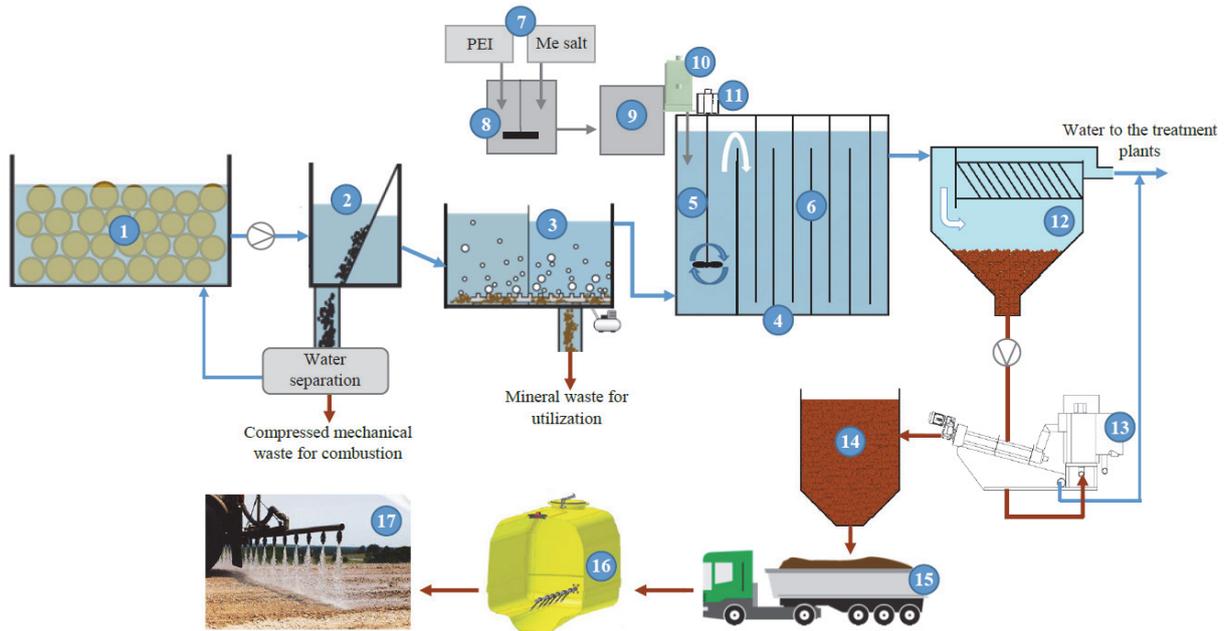


Fig. 21. Scheme of veneer production wood hydrothermal treatment basin wastewater biomass separation and use.

- 1 – wood hydrothermal processing basin; 2 – mechanical grates; 3 – sand catcher;
 4 – coagulation / flocculation tank; 5 – mixing chamber; 6 – aggregate formation chamber;
 7 – solution tanks; 8 – solution mixing tank; 9 – consumption tank;
 10 – composite coagulant batcher; 11 – mechanical stirrer; 12 – settling tank;
 13 – sludge dewatering plant; 14 – sludge storage tank; 15 – sludge transport; 16 – sludge suspension preparation tank; 17 – sludge suspension spraying on the road surface.

With the help of pumps, the wastewater from the wood hydrothermal treatment basin (1) is uniformly supplied to its pre-treatment through mechanical grates (2) to remove various coarse contaminants, mainly bark residues. After the separation, they are supplied to a container, where their compaction and the extraction of water proceed. The compacted bark residues are used as fuel for heaters. The wastewater flow further passes through sand catchers (3) to remove mineral particles. The separated mineral waste is collected in a container from which it is periodically removed for recycling.

After wastewater pre-treatment, it enters the coagulation / flocculation tank (4), where it is purified using the coagulation / flocculation method. At the beginning, rapid mixing of the wastewater and composite coagulate occurs in the mixing chamber (5) to evenly disperse the coagulant in the wastewater volume. For mixing, a propeller mechanical stirrer is used (11). The composite coagulant is added to water by a batcher (10), using a 20–25 % solution. The preparation of the composite coagulant PEI and metal salt solution takes place in separate solution tanks (7), from which they are supplied to the solution mixing tank (8). The finished composite coagulant solution is pumped to the consumption tank (9). After wastewater mixing

with the composite coagulant, it further enters the aggregate formation chamber (6), where the flakes formation process begins. In the labyrinth, the mutual interaction of fine particles increases at a flow rate of 0.1–0.3 m/s, and the agglomeration of particles in dense flakes takes place.

The separation of the wastewater sludge (flakes) is ensured in a settling tank (12). The flow in the settling tank starts at the tank's top and moves to the settling tank's bottom. Next, the water flow is moving again upwards through the plates. As the flow is going through the plates, the flow rate between the plates temporarily increases and then rapidly slows down, allowing the flakes to accumulate and settle, while the purified water flow passes through the plates' outer surface and further, through the settling tank's upper hole, is supplied further to the water treatment plant. The wastewater must stay in the settling tank for at least 60 min.

As the sludge reaches a certain level, it is removed with the help of a pump and is supplied to the sludge dewatering plant (13). The dewatering plant reduces the sludge weight by increasing the dry matter (DM) content, and consequently also the transportation costs. The appliance has two fixed and one mobile plate. The mobile plate rotates during the operation of the screw. The slits between the mobile and stationary plates range from 0.5 to 0.1 mm. The water flows through these slits. As the slits' sizes are constantly changing, the dewatering process occurs smoothly. At the end of the screw, press equipment is attached, which additionally squeezes the water from the sludge and enhances the dewatering efficiency. The incoming sludge flow DM 0.5–1 %, the output flow DM 15–20 % [17]. The separated water is fed to the treatment plant.

After the compaction, the sludge enters the sludge storage tank (14), where it is stored prior to loading in the road transport (15).

The next stage is the use of the biomass separated from the wastewater in gravel road dedusting. The biomass sludge from the storage tank is transported to the application site. Since the biomass sludge suspension is used for processing the road surface, sludge with DM 15–20 % is diluted with water to the desired calculated dedusting composition. The dilution is carried out in the processing transport suspension preparation tank (16). Even mixing is provided by a metal pipe with special nozzles positioned in the middle of the lower part of the tank, which rotates around its axis. The finished suspension is transferred to the watering device (17) and is sprayed evenly across the width of the roadway in accordance with the calculated consumption per area unit of about 1 l/m². After the road surface processing, road replanning with auto graders is carried out to ensure the dedusting reagent's blending.

CONCLUSIONS

The Doctoral Thesis is dedicated to the development of a new composite coagulant for the efficient removal of biomass from veneer production wood hydrothermal treatment wastewater, the characterization of the obtained biomass coagulates and the study on the application possibility of the separated biomass.

From the results of the work, the following conclusions are made.

1. Using the parameters (pH, temperature, dry matter content), which mimic the plywood production birch wood hydrothermal treatment basin wastewater, a model solution is developed, used in the subsequent studies. Analysis of the model solution shows that its biomass contains 75.2 % of hemicellulose fractions, 13.5 % of aromatic type lignin-containing compounds and 11.3 % of various water-soluble destruction products of wood origin.
2. Investigating the biomass removal efficiency using cationic polymers, such as poly(diallyldimethylammonium chloride) (PDADMAC), chitosan and polyethyleneimine (PEI), it is found that the efficient biomass flocculation (1285–1309 mg/l biomass, 126–175 mg/l lignin) occurs in a narrow dosage range that varies depending on the pH and the polymer molecular weight, which indicates the stoichiometric polyelectrolyte complexes' particle formation between the negatively charged lignin and hemicellulose molecules and the positively charged cationic polymer molecules.
3. The optimum pH activity ranges are found, in which cationic polymers have the best biomass and aromatic type lignin-containing compounds' removal efficiency, namely, the PDADMAC pH optimum range is 7–8, while for chitosan and PEI, which are more pH-sensitive polymers, the effective pH range is an acidic medium of pH 5–6.
4. In terms of the biomass removal efficiency, the cationic polymers used may be arranged in the following order: PEI > PDADMAC > chitosan. Based on the flocculation efficiency, the relatively small optimum dosage (25–35 mg/l), the flocculation pH value that is close to the neutral medium (pH 6) and the good sedimentation kinetics, PEI with a high molecular weight is selected as the basic cation-active polymer for the development of a new hybrid composite coagulant.
5. A new hybrid composite coagulant is developed, which is a product of interaction of PEI and polyvalent metal salt, which is formed due to the donor-acceptor interaction between the uncharged nitrogen atoms in imine groups and polyvalent metal ions.
6. The properties of composite coagulant and the efficiency of biomass coagulation / flocculation may vary, changing the PEI and metal salt ratio in the composite coagulant in a narrow range. The optimum component PEI / polyvalent metal salt mass ratios in the hybrid composite coagulant vary in the range from 25/75 to 35/65. At the optimum pH 6 at a dosage of 70–80 mg/l, it is possible to achieve 1353–1358 mg/l, or 97 % of the biomass yield.
7. In the composite coagulant, the efficient dosage of PEI is by about 30–43 % lower than if only PEI is used in the model solution coagulation / flocculation, but the polyvalent metal salt dosage in the composite coagulant is by about 40–55 % lower than that for the composite coagulant on the polyaluminium chloride base (work control), which allows to reduce 2–2.5-fold the concentration of the residual metal ions in the treated water.

8. Adding the composite coagulant to the model solution, the solution pH values varied in the range of 6.0–6.5, that already is the optimum coagulation / flocculation pH and it is not necessary to add NaOH to achieve the required pH, which is a substantial advantage from the reagent-saving and cost point of view.
9. The sizes of the biomass floccules, which are formed with the developed coagulant, range within 1114–1242 nm. At the same time, the sizes of the floccules formed with the PEI flocculant and the polyaluminium chloride composite coagulant are 1.3–1.7 and 2.2–3.7 times lower, respectively.
10. The biomass coagulate separated with the composite coagulant is in a gel form with a heterogeneous chemical composition and structure, which is characterized by a high moisture content (98.7 %; after centrifugation – 93 %).
11. The separated biomass is capable of structuring dusty soil and forming aggregates that are mechanically resistant against wind erosion, with the optimum content of biomass in the soil of 0.8 %. With increasing clay content in the soil, the aggregates' content grows rapidly, the fine fraction quantity decreases and the proportion of the coarse fraction grows.
12. A version of the technological scheme for the separation and use of the veneer production wood hydrothermal treatment basin wastewater biomass is offered.

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APPROBATION OF THESIS

The results of the Doctoral Thesis are approbated in 12 full papers and at 10 international scientific conferences; 1 LV Patent application is filed.

Papers in journals and full text publications in conference proceedings

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