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Woodworking wastewater biomass effective separation and its recovery

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Abstract. The aim of the study was to develop a new Al-based hybrid coagulant that was effective in removing wood biomass from the wastewater formed in water basins of plywood plants during hydrothermal treatment of birch wood. The organic-inorganic coagulant was prepared by interaction of high molecular polyethyleneimine (PEI) with the inorganic polyaluminium chloride-based composite coagulant (KHPAC) in aqueous medium. Owing to the hybrid nature, the developed coagulant could simultaneously perform both the coagulation and flocculation function. The influence of a hybrid coagulant composition, its dosage, pH and a temperature on the efficiency of wastewater biomass separation was investigated. The best coagulation-flocculation efficiency was achieved with the hybrid coagulant having a mass ratio of PEI/KHPAC equal to 0.3–0.5 and at the optimal dosage of 70–80 mg L^{-1}, reaching 97% yield of the total wood biomass and 60% yield of the lignin recovery. The efficient dosage of PEI and KHPAC in hybrid coagulant was about 1.4–1.8 and 1.7–2.2 times lower than if these coagulants/flocculants were used alone. As a result of the coagulation-flocculation process, wood biomass sludge is formed, which is a sufficiently large source of renewable organic matter, with the potential to obtain value-added products. The components of the biomass sludge were found to have surface activity and binder properties, as well as cation exchange capacity. Based on these properties, its ability to structure dusty soil particles with the formation of mechanically resistant soil aggregates was studied.

Key words: al-based hybrid coagulant, coagulation/flocculation, soil structuring, woodworking wastewater.

INTRODUCTION

The production of veneer in Latvia and many countries of East Europe is accomplished by the hydrothermal treatment of hardwood in special open water basins for 16–18 h at a temperature of 40–60 °C. The formed wastewater contains very high concentrations of water-soluble wood extractives, hemicelluloses and lignin compounds. Lignin and its derivatives can form highly toxic compounds and are responsible for the high chemical oxygen demand (COD) (Ali & Sreekrishnan, 2001). Therefore, the effluent from the wood hydrothermal treatment basins needs to be treated before being discharged. A part of the wood processing enterprises does not have centralized wastewater treatment plants, and the applied technologies provide only the wastewater dilution and discharge to sewerage networks. However, in order to gain maximum benefit according to Circular Bioeconomy, 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. It is a large enough source of renewable organic substances with the potential to obtain value added products on the basis of wood wastewater biomass. Wastewater treatment by-products are basically eliminated by the combustion method for energy production (Spinosa et al., 2011). As sludge contains a variety of nutrients for plants, so it is widely used in agriculture (39% of sewage sludge produced in the European Union) as fertilizer to improve growing conditions (Lazdina et al., 2011; Kumar et al., 2017; Zapałowska et al., 2020). The use of wastewater sludge in the production of sorbents (Lin et al., 2014; Brovkina et al., 2020) and construction materials (Sales et al., 2011; Soucy et al., 2014) is also studied.

Since the wood hydrothermal treatment wastewater biomass sludge contains large quantities of hemicellulose and lignin compounds, having surface activity and binder properties as well as cation exchange capacity, this biomass can have the potential use in soil structuring and dust road control. Worldwide, for unpaved road dust control, calcium and magnesium chlorides as well as synthetic polymer binders are widely used. However, they are relatively expensive, have the low weather resistance, and some of them are not environmentally friendly (Addo et al., 2004). At the same time, dust suppressors based on a wood polymer such as lignin are eco-sound and widely used (Dustex, Earthbind 100, Nodust, Road Loc), especially in North America.

The most applied methods for removal of various suspended and colloidal pollutants from wastewater are coagulation and flocculation. High charges cations, such as Fe^{3+} or Al^{3+}, are some of the most effective reagents for destabilizing the colloids. Therefore, polyvalent inorganic salts such as $AlCl_3$, $Al_2(SO_4)_3$, $FeCl_3$, $Fe_2(SO_4)_3$ are widely used as coagulants (Ahmad et al., 2008). Different cationic and anionic polyelectrolytes are widely used as flocculants in wastewater treatment (Gregory & Barany, 2011). Currently, the research in the field of coagulation-flocculation process is focused on the development of more effective and less expensive hybrid composite materials, which are constituted of both inorganic and organic compounds, in view of their better performance compared to that of conventional inorganic-based coagulants, and their lower cost compared to organic-based flocculants (Lee et al., 2011). The hybrid composite materials are reported to be more efficient compared to conventional inorganic coagulants due to the synergism effect of two components in one composite material (Yang et al., 2004; Lee et al., 2012). Furthermore, the application of the inorganic-organic composite materials in the wastewater treatment required only one-unit operation in comparison with the bioperational system: at first, coagulation, then, flocculation (Lee et al., 2011).

The aim of this study was to develop a new Al-based hybrid coagulant that is effective in removing biomass from the wastewater of wood hydrothermal treatment, formed during veneer production, and to study the efficiency of its composition, dosage, pH and a temperature on wastewater biomass separation and purification quality of the treated wastewater. The possibility of the separated biomass sludge to structure dusty soil was investigated.

MATERIALS AND METHODS

Model system

Taking into account the fact that the composition of the birch wood pre-treatment wastewater obtained in veneer production is inconstant, for the investigation of the coagulation/flocculation process, a model system of the wastewater with unambiguous and stable characteristics was chosen (Vitolina et al., 2014). The model wastewater (MW) was obtained by a hydrothermal treatment of birch sawdust performed with 0.01M NaOH at a hydromodulus of 1/50 (a mass ratio of the oven dry sawdust to water) and a temperature of 90 °C for 4 h. After the treatment, the obtained model solution was separated from the sawdust treated through a filtration. The main parameters of the MW are listed in the Table 1.

Table 1. Parameters of model wastewater

pH	Biomass content, mg L^{-1}	Density, g cm^{-3}	COD, mgO L^{-1}	PI, mgO L^{-1}	Color, mg LPt^{-1}
9.0–9.1	1,400 ± 67	0.998	1,285 ± 30	320 ± 10	746 ± 19

The defined elemental composition of the dried biomass was the following: 37.75% C; 4.78% H; 56.69% O; 0.30% N; 0.14% S, 0.34% of inorganic matter. The obtained results of the biomass fractionation showed that the content of the lignin and hemicelluloses fractions in the solid biomass corresponded to 13.5% and 75.2%, respectively, but other water-soluble products of the wood matrix destruction were 11.3%. The main component of water-soluble hemicelluloses in the wastewater was xylan (Shulga et al., 2012). The zeta potential value of the hydrolysate close to - 30 mV testified the high stability and the enhanced content of charged functional groups in the biomass. With decreasing pH to 2.0, the Z potential value of the hydrolysate fell to - 10 mV, reflecting the decrease in the ionisation degree of the hydroxyl and carboxyl groups in the water-soluble lignin and hemicelluloses fragments.

Coagulants/flocculants

To select the most appropriate cationic polyelectrolyte for development of a new inorganic-organic coagulant, the efficiency of various commercial cationic polyelectrolytes as flocculants for wood biomass separation from the model wastewater was investigated. Three different cationic polyelectrolytes including polyethyleneimine (PEI), polydiallyldimethylammonium chloride (PDADMAC) and chitosan with different molecular weights were examined for estimation of the efficiency of biomass removal (Table 2). All polyelectrolytes were purchased from Sigma-Aldrich.

Table 2. The polyelectrolytes used

Polyelectrolytes	Molecular weight (g mol^{-1})
PDADMAC $_{LMW}$	100,000–200,000
PDADMAC $_{MMW}$	200,000–350,000
PDADMAC $_{HMW}$	400,000–500,000
Chitosan $_{LMW}$	200,000
Chitosan $_{MMW}$	350,000
Chitosan $_{HMW}$	500,000
PEI $_{LMW}$	1,300
PEI $_{HMW}$	750,000

A polyelectrolyte which showed the best biomass flocculation efficiency was selected as an organic component of the new hybrid coagulant. As an inorganic component, the previously developed Al-based inorganic composite coagulant

(KHPAC) based on polyaluminium chloride (PAC) and aluminium chloride ($AlCl_3$) (Shulga et al., 2014) was used. Polyaluminium chloride (Polypacs-30) (30% Al_2O_3, 80–85% basicity) was purchased from the Industrial Holding AMK-Group (Russia). A composition of the hybrid coagulant was represented as the mass ratio of a cationic polyelectrolyte to KHPAC that varies in the range of 0.15–1.0. All the used reagents were of analytical grade.

Coagulation/flocculation experiment

The coagulation process was carried out in a jar by mixing the equal volumes of the MW and a coagulant/flocculant solutions and stirring the obtained suspension with a magnetic stirring bar at 200 rpm for 1 min, followed by slow mixing at 40 rpm for 2 min. A coagulant/flocculant dosage was added to the MW solution in the range of 10–140 mg L^{-1}. The Experiments were conducted at pH values ranging from 3 to 10 by addition of HCl or NaOH and in the temperature range of 13–60 °C using a thermostat. The flocs formed were allowed to settle for 120 min. After sedimentation and filtration MW samples were taken for analysis. Each experiment was carried out three times. The results are presented as mean values. The effectiveness of the coagulant/flocculant was measured based on the removal of total wastewater biomass and one of the wood components - lignin that contributes to color pollution in wastewater and removing lignin-containing substances is comparatively difficult. The residual concentration of the biomass and water-soluble lignin and lignin substances was defined by measuring the obtained filtrate's optical density at 490 and 280 nm using the previously obtained correlation curves for the biomass and lignin. Color and chemical oxygen demand (COD) was measured according to the ISO 7887:1994 and ISO 6060:1989, respectively. The coagulation/flocculation efficiency was determined, comparing the initial parameters of the model solution with the parameters obtained for the filtrate after coagulation/flocculation, using the following formula (Eq. 1):

$$\text{removal}\,(\%) = \left(\frac{C_i - C_f}{C_i}\right)\cdot 100, \qquad (1)$$

where C_i and C_f are initial and final concentrations of wood biomass, water-soluble lignin and lignin substances, chemical oxygen demand and color. Sludge volume index (SVI) was calculated by dividing the settleability (settled sludge volume after 30 minutes) by the suspended solids concentration. The zeta potential and particle size measurements were obtained by using Malvern Zetasizer Nano Series model SZ machine.

Soil structuring experiment

Soil structuring experiments were conducted using a dusty sand/clay model soil with a clay fraction content varied from 0–70%. Clay for this study was taken from Lielauces quarternary clay deposit (Latvia), but sand was taken from Baltic Sea cost. The average chemical composition and the average particle size distribution of the used clay and sand soil are given in Table 3 and Table 4, respectively.

Table 3. Average chemical composition of clay (%)

SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	CO_2	K_2O	Na_2O	SO_3
45.47	12.27	5.34	0.67	11.60	4.87	11.22	4.04	0.52	< 0.1

Table 4. Average particle size distribution of sand and clay (%)

Sample	> 0.25 mm	0.25–0.05 mm	0.05–0.01 mm	< 0.01 mm
Sand	3.1	93.7	0.3	3.0
Clay	2.3	9.6	26.3	63.4

In the work, the model soil particles less than 0.25 mm were used. The soil aggregates (> 0.25 mm) were obtained by manual mixing the soil with 1.0–5.0 g dL^{-1} biomass water suspensions during 3 minutes. The used wood biomass had a gel form with content of a dry matter about 10% and was obtained by centrifugation of the precipitated biomass sludge at 6,000 rpm during 20 min without its followed drying. The water suspensions with the defined biomass concentration were prepared by intensive mixing the biomass gel with water at 100 rpm for 10 min using a mechanical mixer. The content of the biomass in the soil samples varied from 0.2% to 0.8% on their dry matter. The fractional composition of the dried structured soil was determined by dry sieving, using a set of sieves (AS200 Retsch). Each experiment was carried out three times. The results are presented as mean values.

RESULTS AND DISCUSSION

Biomass removal by coagulation-flocculation

Using the cationic polyelectrolytes (Table 2) 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 hybrid composite coagulant. It is known that water-soluble low-molecular weight lignins and hemicelluloses interact with cationic polyelectrolytes in aqueous medium mainly via the electrostatic mechanism (Ström & Stenius, 1981; Shulga et al., 2002; Mocchiutti et al., 2016). As a result of the electrostatic interaction between the cationic polyelectrolytes and the biomass components, polyelectrolyte complexes (PEC) (Li & Pelton, 1992; Shulga et al., 2009) are formed (Fig. 1). The formation of insoluble PEC occurs at the stoichiometric mass ratio of the interacted components. If the applied dosage of the cationic polyelectrolyte is less or greater than the effective dosage, corresponded the stoichiometric mass ratio of the polyelectrolyte and hemicelluloses/lignin, wastewater biomass does not flocculate due to the formation of water-soluble non-stoichiometric PEC particles.

The results of the flocculation experiments with PDADMAC showed that the optimal pH range for the efficient biomass removal was pH 7–8 with an optimal dosage of 50 mg L^{-1}, at which the total biomass and lignin removal reached 1,288 mg L^{-1} or 92% and 171 mg L^{-1} or 55%, respectively. It was determined that the molecular weight of PDADMAC practically did not affect its efficiency. The biomass removal efficiency of PDADMAC with a molecular weight of 200,000–350,000 g mol^{-1} was only 1.5% better than that for $PDADMAC_{LMW}$ and $PDADMAC_{HMW}$.

Compared to PDADMAC, chitosan is a more pH-sensitive polymer and works effectively only in acidic conditions due to the presence of amino groups. It is known that 96–97% of its amino groups are protonated at pH 5, while only 7–10% of amino groups are protonated at pH 7.5 (Van Haute et al., 2015). The protonation also results in a change in the structure of the chitosan molecule from a compact in weak alkaline medium to elongated conformation as a result of the electrostatic repulsion between the polymeric chains. It was found that the optimal conditions for the formation of stable biomass flocs in the case of chitosan were the following: the pH values varied from 4 to 5 at the optimal dosage of 35 mg L^{-1}. The total biomass yield was of 1,285 mg L^{-1} or 92%, but lignin recovery was closed to 126 mg L^{-1} or 41%. In the case of chitosan, a molecular weight effect on flocculation efficiency is observed. At the same optimal dosage and pH, chitosan with medium and low molecular weight shows on average 3% better biomass removal efficiency and 11–13% increase in lignin removal compared to high molecular weight chitosan samples.

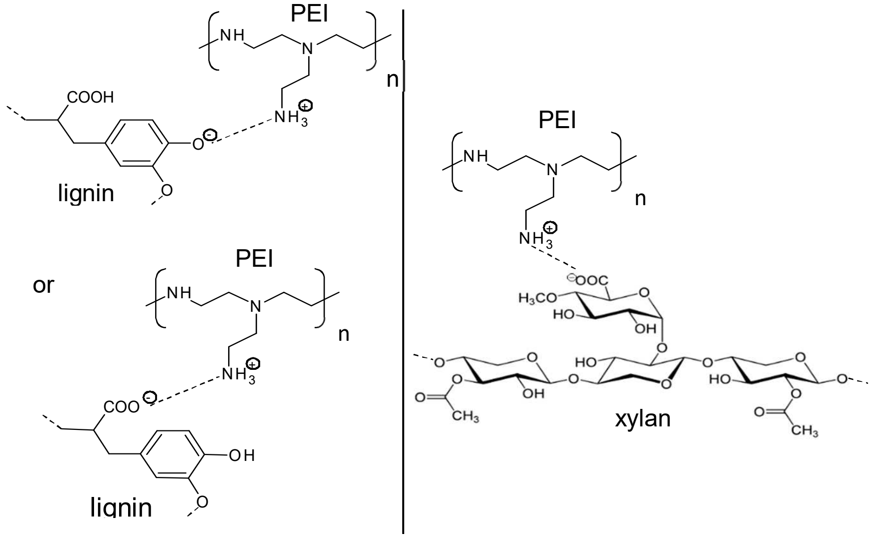

Figure 1. Simplified possible electrostatic interaction pathway between PEI and the main biomass components (lignin and xylan) in the formation polyelectrolyte complexes.

PEI like chitosan is a pH-sensitive polymer which acts as a proton sponge in acidic conditions. The pH medium also affects the PEI structure that has an impact on the interaction with the wastewater biomass components. At basic medium PEI molecules are weakly protonated and have a highly coiled structure, while at acidic conditions the molecules chains are highly protonated and elongated (Choudhurya & Roy, 2013). Our results showed that the optimal conditions for PEI with low molecular weight for the flocculation of the model wastewater were the following: the dosage of 14–20 mg L^{-1} and pH 4–5. To achieve the best biomass and lignin removal efficiency with the high-molecular weight PEI a larger dosage was required. The defined optimal PEI_{HMW} dosage was 25–35 mg L^{-1} at pH 6. At the defined optimal conditions PEI_{HMW} shows 4% higher biomass and 11% better lignin removal efficiency than PEI_{LMW}.

Table 5 shows that the total biomass removal efficiency does not differ significantly for all the polyelectrolytes and achieves 91–93%. At the same time, there are significant differences in the lignin extraction efficiency. Chitosan is the worst flocculant for water-soluble lignin and lignin-containing substances. Its efficiency is by 16–18% lower than for PDADMAC and PEI and directly correlates with the MW color reduction. An important coagulation/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 optimal pH values of the biomass flocculation with PEI lied within the optimal pH range of coagulation with Al-based coagulants (Brovkina et al., 2020), which was important for the development of a new hybrid composite coagulant.

Table 5. Efficiency of the investigated cationic polymers at optimal parameters

Parameters	PDADMAC	Chitosan	PEI
Molecular weight	medium	medium	high
Optimal dosage, mg L^{-1}	50	35	35
Optimal pH	8	5	6
Biomass, mg	1,288	1,285	1,309
Lignin, mg	171	126	175
Color removal, %	88.6	85.2	91.4
COD removal, %	39.2	41.9	44.0

Based on the comparison of obtained results (Table 5), high molecular weight PEI, which showed the best flocculation ability among the studied polyelectrolytes, was selected as an organic component of the new hybrid composite coagulant. The polyaluminium-based composite coagulant - KHPAC, shown higher coagulation ability than other Al-based salts (Brovkina et al., 2020), was chosen as an inorganic component of the composite. The composite coagulant PEI-KHPAC in the polymer colloidal complex form is formed due to the donor-acceptor interaction between the uncharged nitrogen atoms in imine groups and aluminium ions. Taking into account the hydration shell around the aluminium ions, the complex is stabilized with hydrogen bonds (Vitolina, 2018). Owing to the hybrid nature, comprising an organic flocculant and an inorganic coagulant, the obtained hybrid coagulant should simultaneously perform both coagulation and flocculation function. This could increase the biomass removal efficiency and simultaneously reduce the optimal dosage relative to PEI and KHPAC, if they act separately.

The coagulation-flocculation process with the developed hybrid coagulant can be described as the adsorption of hemicelluloses and lignin fragments on the PEI-KHPAC particle surface as a result of the neutralization of biomass surface polar groups (–OH and –COOH) and PEI-KHPAC positively charged surface amino groups, followed by the aggregation of biomass coagulated particles, owing to the 'bridge formation' mechanism. The bridging mechanism can be explained by the presence of loops and tail in the PEI chains, included in the formation of the PEI-KHPAC, and, when another biomass molecule (with free absorption centers) comes across these 'defects', binding takes place and the biomass flocs are formed.

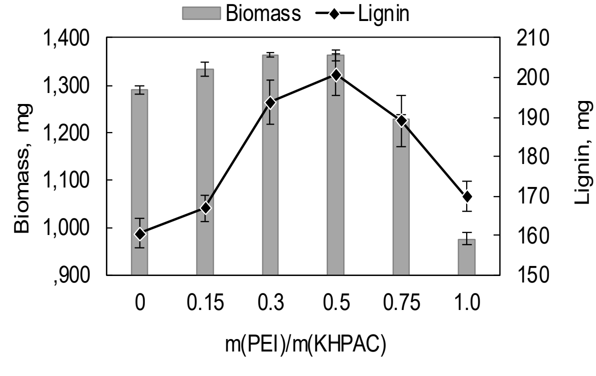

Figure 2. Total biomass and lignin removal efficiency as a function of composite mass ratio of PEI/KHPAC; pH 6, dosage-100 mg L^{-1}, 20 °C.

The treatment effect of the model wastewater with PEI-KHPAC, prepared with the different mass ratio of PEI to KHPAC, at pH 6 is shown in Fig. 2. The obtained results show that PEI-KHPAC is characterised by the highest efficiency when the ratio of PEI to KHPAC changes in the range of 0.3–0.5. Herewith, the removal rates of the biomass and lignin reached 1,364 mg L^{-1} and 194–201 mg L^{-1}, respectively.

Fig. 3 shows average particle diameter and zeta potentials for the nanoparticles of PEI-KHPAC and its components - PEI and KHPAC in water solutions. Compared with the case of KHPAC and PEI, the nanoparticles of PEI-KHPAC 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 aluminium ions.

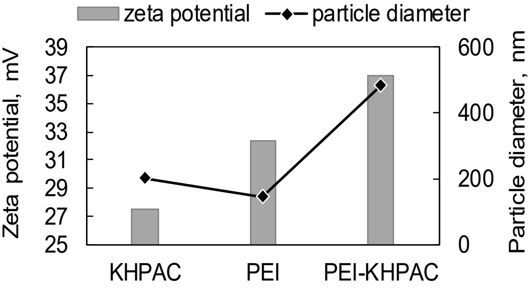

Figure 3. Zeta potential and average particle diameter of PEI-KHPAC and its components; composite mass ratio 0.5.

The pH of wastewater is one of the important factors affecting the coagulation-flocculation efficiency. The coagulation-flocculation performance of PEI-KHPAC was studied in the pH range of 5–8. Fig. 4 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. PEI-KHPAC demonstrates the best efficiency of the lignin extraction at pH 6–7. Based on the obtained results, it was concluded that pH 6 is the optimal medium for the treatment of MW with PEI-KHPAC.

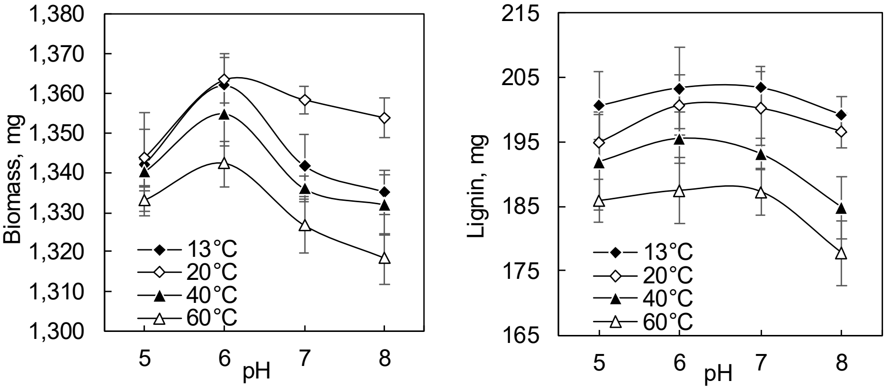

Figure 4. Total biomass and lignin removal efficiency with PEI-KHPAC as a function pH and temperature; composite mass ratio 0.5, dosage-100 mg L^{-1}.

Since the coagulation-flocculation process is sensitive to temperature changes (Sahu & Chaudhari, 2013), the comparative efficiency of PEI-KHPAC in the temperature range of 13–60 °C was investigated. According to Fig. 4, the drop of temperature below 20 °C practically does not affect the biomass yield values at pH 6, but, with increasing pH more than 6, the efficiency of the treatment with PEI-KHPAC sufficiently decreases. The growth of the temperature up to 40 and 60 °C worsens the efficiency of the coagulation-flocculation process that can be explained by the dependence of dissociation degrees of the hemicelluloses/lignin components of the wood biomass on a temperature. It is seen (Fig. 4) that the best yield of lignin is at 13 °C, which is consistent with the fact that at lower temperatures the ionisation of the phenolic hydroxyl groups is favourable (Norgren & Lindström, 2000).

The efficiency of the biomass and lignin removal with PEI-KHPAC, having various mass ratio of PEI to KHPAC equal to 0.3 and 0.5, respectively, in comparison with KHPAC was studied at pH 6 by varying the coagulants dosage (Fig. 5).

It is shown that the hybrid coagulant is characterised by a higher yield both the biomass and lignin than the inorganic coagulant at the same dosages. A similar trend of the dependence of the biomass and lignin yield on the applied dosage is observed for both compositions of PEI-KHPAC, namely, the biomass and lignin removal increases to a maximum value and then decreases with the dosage growing. This is consistent with the fact that a certain dosage of the coagulant PEI-KHPAC is needed to provide the stoichiometric mass ratio of the coagulant to the hemicelluloses/ lignin components in the model wastewater. According to Fig. 5, with increasing PEI-KHPAC dosage from 40 to 70 mg L^{-1}, the biomass yield increases, reaching 1,353–1,358 mg L^{-1} or 97%. The effect of further increasing the dosage on the removed biomass quantity is not pronounced, and already at a dosage > 100 mg L^{-1} the coagulant efficiency decreases. In the case of lignin, the removal efficiency increases linearly with the coagulant dosage and achieves the maximal value at 100 mg L^{-1} for PEI-KHPAC composition of 0.5 and 120 mg L^{-1} for the composition of 0.3, reaching a 201–203 mg L^{-1} lignin yield or 65%.

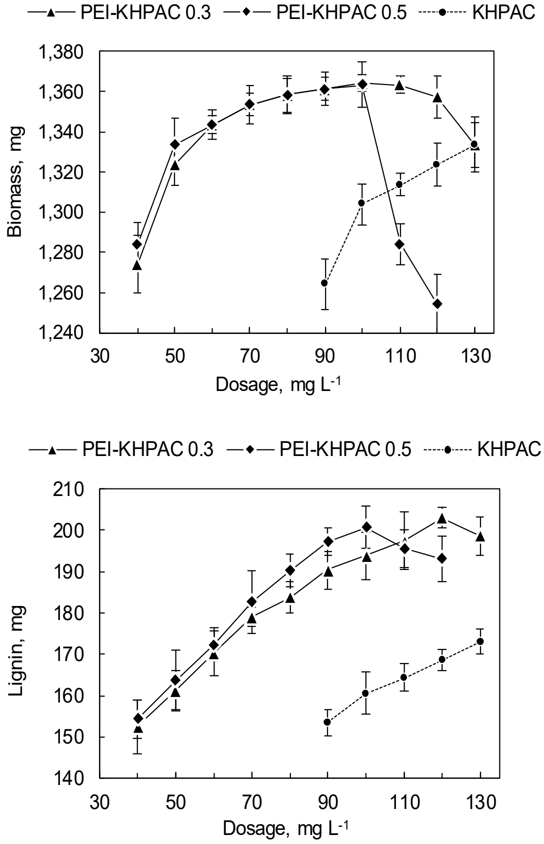

Figure 5. Total biomass and lignin removal efficiency of the coagulants as a function of dosage; pH 6, 20 °C.

Fig. 6 shows the changes in the MW absorption over time as a function of PEI-KHPAC dosage. The initial MW absorption increases with the increase of PEI-KHPAC dosage, reaching a maximal value at a dosage of 110 mg L^{-1}. As follows from the Fig. 6, the sedimentation process of the formed flocs is practically realized within 30 minutes at PEI-KHPAC dosage range of 40–100 mg L^{-1} and is accompanied by the formation of the dense sludge at the bottom of the cylinders (Fig. 6, a). The obtained filtrates of the treated model wastewater were visually transparent in colour at the optimal applied dosages. The performed analysis of the sizes of the formed flocs showed that, after 30 min of the coagulation-flocculation process, their diameter varied in the range of 1,114–1,242 nm. At the same time, the sizes of the flocs formed with PEI and KHPAC applied separately were significantly lower, i.e. 664–842 nm and 331–499 nm, respectively.

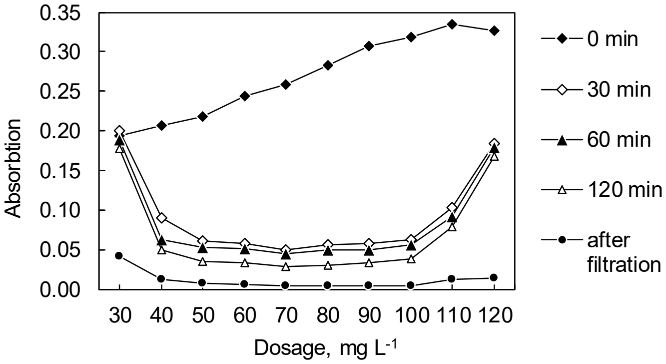

Figure 6. MW absorption (490 nm) changes during coagulation-flocculation process as a function of time and PEI-KHPAC dosage; composite mass ratio - 0.5, pH 6, 20 °C.

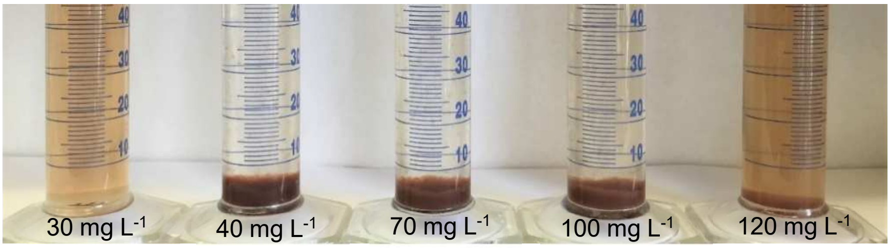

Figure 6a. Settlement of flocs during the coagulation-flocculation process after 30 min using PEI-KHPAC with various applied dosages; composite mass ratio 0.5, pH 6.

The zeta potential profiles for the MW after coagulation with PEI-KHPAC and KHPAC as the function of a dosage at pH 6 are presented in Fig. 7.

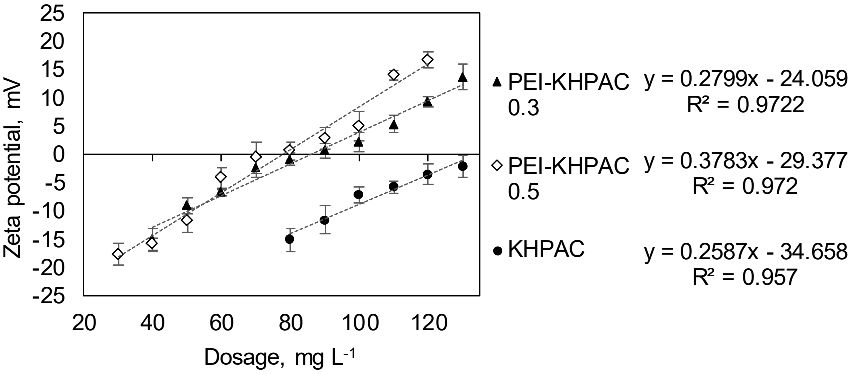

Figure 7. Zeta potential profiles for the MW at pH 6 after coagulation with PEI-KHPAC and KHPAC as a function of coagulant dosage.

According to Pefferkorm (2006), if the charge neutralization is the only path for coagulation, the zeta potential should be in excellent correlation with the coagulant dosage, and the optimal efficiency is achieved when zeta potential is close to zero. It can be seen that the zeta potential changes correlate very well with the applied coagulants dosages. There is a linear correlation ($R > 0.97$) between the filtrate zeta potential and the applied dosages of PEI-KHPAC with a mass ratio of 0.3 and 0.5. This indicates that the formation of the flocs mostly occurs according to the charge neutralization mechanism, because the maximal yield of the wood biomass is reached when the zeta potential of the treated MW is close to zero. It can be seen (Fig. 7) that, for the both compositions of PEI-KHPAC, the negative values of a zeta potential for the filtrates, formed after the MW treatment, exceed zero at the applied dosages more than 70–80 mg L^{-1}. With the further increasing the dosage of the coagulant, the zeta potential of the filtrates increases, but the biomass removal efficiency no longer grows significantly, which can point to the composite coagulant dosage excess. In turn, for KHPAC, in the range of 30–130 mg L^{-1} of the applied dosage, the filtrate zeta potential still remains negative, which indicates that the complete neutralization of biomass particles has not yet occurred.

Table 6 shows a comparison of the optimal parameters (dosage, pH) and efficiency (biomass and lignin yield, the color of treated MW, COD, etc.) of the coagulation-flocculation process at 20 °C using the KHPAC and the hybrid coagulant PEI-KHPAC with two compositions.

Table 6. Efficiency of coagulants at optimal parameters

Parameters	KHPAC	PEI-KHPAC$_{0.3}$	PEI-KHPAC$_{0.5}$
Optimal	100	80	70
Optimal pH	6	6	6
Biomass, mg	1,304	1358	1,353
Lignin, mg	161	184	183
Color removal, %	85.4	89.8	89.3
COD removal, %	46.7	49.7	47.8
Aluminium	0.063	0.032	0.025
SVI, mL g^{-1}	107	74	74

In accordance with the data in Table 6, the yield of the biomass and lignin using the hybrid coagulant at the optimal dosage is higher by 4.1% and 14.3% compared with KHPAC, who's the optimal dosage is by 25–43% higher than that in the case of the hybrid coagulant. It is known that residual aluminium concentration in wastewater is a very important parameter from health perspectives and should be carefully considered, when an aluminium coagulant is applied in the water treatment. Since the aluminium salt content in the hybrid coagulant is 1.7–2.2 times lower than in KHPAC, the concentration of residual aluminium in the filtrate is essentially decreased. The performed study showed that the concentration of residual aluminium ions in the filtrates of the MW treated with the hybrid coagulant was 2–2.5 times lower than that in the filtrates after the treatment with KHPAC. Higher rates of the biomass and lignin yield when treating the MW with the hybrid coagulant lead to the increase in such important indicators of wastewater treatment as color removal and COD removal in comparison with those for the inorganic coagulant. The developed coagulant PEI-KHPAC is characterized also by a good sedimentation kinetic, which is confirmed by the sludge volume index (SVI) values. For PEI-KHPAC, this index is lower than 100 mL g^{-1}, which is an important parameter from the technological point of view. It is known that when adding aluminium salt coagulant, a pH value of the treated wastewater decreases, and its decrease depends on the initial pH value of the wastewater. In this study, we have found that by adding the optimal KHPAC dosage to the MW, a pH value of the MW decreases from pH 9 to pH 4. In order to achieve the optimal coagulation pH 6, it was necessary to add sodium hydroxide to the MW. In turn, by using the optimal dosages of PEI-KHPAC, the pH values of MW varied in the range of 6.0–6.5, which already was the optimal value for the coagulation/flocculation process. Such a manner, it is not necessary to add alkali to achieve the required pH that is a substantial advantage from the reagent-saving, cost and technology viewpoint.

Use of biomass sludge in soil structuring

Since the surface of the precipitated biomass contains both completely hydrophobic regions, which are formed as a result of the interaction of the biomass components with the PEI-KHPAC hybrid coagulant, and free functional groups (carboxyl-, hydroxyl-, amino-), which are located in the coagulate segments (e.g., tails, loops), the separated biomass particles have to exhibit binding properties. Taking into account a possible application of the separated biomass, its ability to structure dusty soil particles with the formation mechanically resistant soil aggregates was studied. It was supposed that the wastewater biomass can adsorb on the sandy soil particles due to physicochemical interactions, including Van der Waals forces and hydrogen bonds between Si-OH groups of the soil and the biomass particles' carboxyl-, hydroxyl- and amino groups, locating in the biomass coagulate segments. With the increase of the clay particles content in the model soil composition, besides hydrogen bonds and Van der Waals forces, the contribution of the hydrophobic interaction between the biomass and the soil particles should increase.

The precipitated biomass was used after the centrifugation in a wet state (a moisture content is 93%), without its drying. The biomass suspensions with a defined concentration were obtained by diluting the biomass with water and actively mixing them with the mechanical mixer during for 10 min. As dusty soil samples, a sandy soil and a model sand/clay soil with the clay content from 30% to 70% and the soil particles < 0.25 mm were used.

An important parameter that shows effectiveness of the application of the structure forming agent is a fractional composition of the treated soil. The fractional composition of the sandy soil treated with the biomass suspensions as a function of the content of biomass is given in Fig. 8.

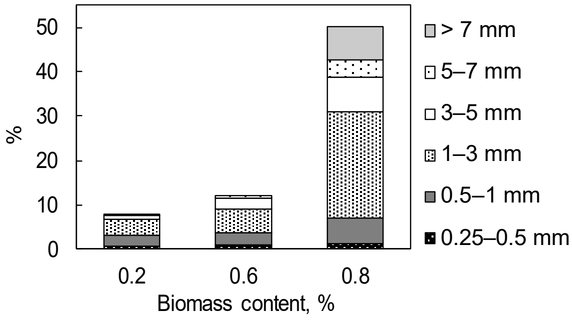

Figure 8. Fractional composition of the treated sandy soil as a function of the content of biomass sludge.

It can be seen that, with increasing the content of the biomass, the amount of the soil aggregates in the fractional composition increases from 10% to 50%. The growth of the amount of the soil aggregates is also accompanied by their sizes enhancement. It can be seen that the main fraction (more than 50%) in the aggregated sandy soil part is a medium-sized one with a diameter of 1–3 mm, which essentially grows with increasing the biomass content from 0.2% to 0.8%.

The structuring the model sand/clay soil shows that, with increasing the clay content in the soil, the soil aggregate amount remarkably increases and shifts to a higher content of the large soil species (Fig. 9). Using the model soil with 70% clay content, the amount of the aggregates achieves 98% of the soil mass at the 0.8% biomass content (Fig. 10) and that is 48% higher than the total aggregate mass in the treated sandy soil at the same biomass content. Compared with the treated sandy soil, where the amount of the large soil aggregates (> 3 mm) represents 38% of all aggregates formed, this amount in the model sand/clay soil grows to 57–85% with increasing the content of the clay from 30% to 70%.

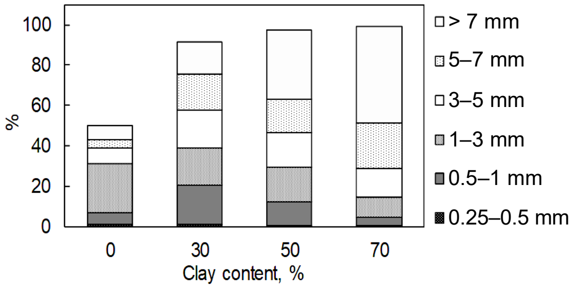

Figure 9. Fractional composition of the treated sand soil as a function of the clay content in the soil, biomass concentration 0.8%.

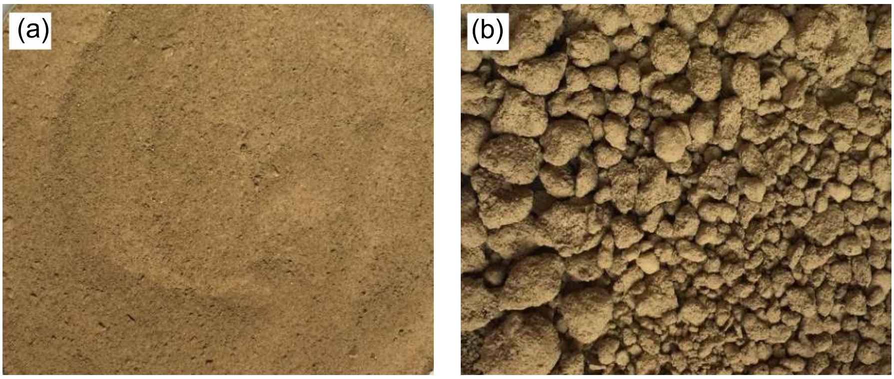

Figure 10. Model soil before (a) and after (b) structuring with precipitated wastewater biomass, clay content 70%, biomass concentration 0.8%.

For the comparative assessment of the wastewater biomass capacity to structure soil, softwood lignosuphonates (LS), a wood chemical processing by-product, which is widely used as a dust suppressor for control unpaved road (Addo et al., 2004), were selected. LS were characterised by the following empirical formula of the phenyl-propane chain: $C_9H_{6.89}O_{2.57}(OCH_3)_{0.71}\ (SO_3)_{0.35}(OHph)_{0.68}(CO)_{0.36}$. The average weight molecular mass of LS calculated from its viscosimetric data in 0.1 M NaCl was equal to 28,000 g mol^{-1}. According to Fig. 11, when treating the soil with the biomass suspension, the total soil aggregate content is equal to 50% of the soil mass, while using the LS, the amount of the aggregates is higher and accounts for 70% of the soil mass. However, the comparison of the fractional compositions of the both treated soil samples shows that the separated biomass is capable of forming aggregates of a larger diameter than LS at the same content in the soil. Aggregated part of the soil samples structured with LS are primarily composed of the fraction with a diameter of 0.5–1 mm representing 32% of total soil mass, but the samples structured with the separated biomass contain mainly the fraction with the larger size aggregates with a diameter of 1–3 mm, which is 24% of total soil mass. A higher content of large soil aggregates formed by the separated wood biomass could positively effect on the wind erosion resistance of dusty soils.

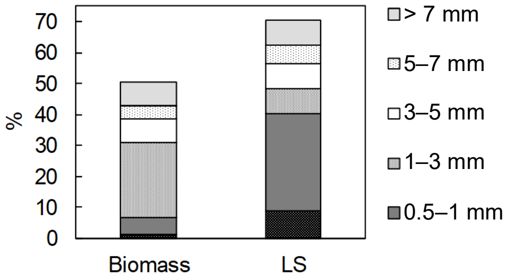

Figure 11. Fractional composition of the sand soil treated with the separated biomass and lignosulphonate, biomass concentration 0.8%.

CONCLUSIONS

This study successfully proved the effectiveness of the developed hybrid coagulant, formed as a result of the interaction between high molecular PEI and the polyaluminium-based composite coagulant (KHPAC), in separation of the wood biomass from the model solution, simulating wastewater of a woodworking enterprise. It is concluded that the properties of the new coagulant and its coagulation-flocculation efficiency may vary, changing its composition in a narrow range. Using the model wastewater, it was found that the best coagulation-flocculation efficiency is observed for the hybrid coagulant with a mass ratio (PEI/KHPAC) of 0.3–0.5 at the optimal dosage of 70–80 mg L^{-1} and pH 6. At these parameters, the yield of the total wood biomass and lignin reaches 97% and 60%, respectively, color and COD removal close to 90% and 50%, respectively. The efficient dosage of PEI and KHPAC in hybrid coagulant is about 1.4–1.8 and 1.7–2.2 times lower than if coagulants/flocculants are used alone, but the content of the residual aluminium ions in the model wastewater filtrate is 2–2.5 times lower than that for the KHPAC coagulant.

The results of soil structuring experiments show that the separated wastewater biomass is capable of structuring dusty soil and to form soil aggregates. With increasing the clay content in the soil composition, the total aggregates' content in the soil essentially grows, wherein the amount of fine aggregates fraction decreases and the amount of the coarse aggregates fraction enhances.

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