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The efficiency of biomass removal from model woodworking wastewater with polyethylenimine

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Abstract

The production of veneer in Latvia and many countries of Eastern Europe is accomplished by the hydrothermal treatment of hardwood in special water basins. As a result, formed effluents contain wood-originated pollutants which are responsible for the enhanced chemical oxygen demand and the intensive color of the wastewater. Keeping in mind the zero waste policy for rational use of bioresources and the possible usage of waste wood originated matter in practice, it is very important to extract the formed biomass from the basin's wastewater. In this work, for imitating woodworking wastewater, birch sawdust was hydrothermally treated in mild alkaline conditions at 90°C. The yield of the solid biomass did not exceed 7% and contained, mainly, hemicelluloses in the polysaccharide form and lignin. The applied instrumental analysis methods (FTIR and UV-spectroscopy, HPLC, ¹³C-NMR) testify the dominant content of hemicelluloses in the obtained biomass. The results of fractionation of the biomass have indicated that the content of lignin, hemicelluloses and water-soluble degraded wood products in the solid biomass corresponds to the following mass ratio: 1.2/6.7/1.0, respectively.

The effectiveness of the isolation of wood biomass from the hydrolysate with polyethyleneimine (PEI) was studied. In coagulation–flocculation process using single coagulant, coagulant dosage and pH plays an important role in determining the coagulation efficiency. At the optimum PEI dosage of 35 mg/L and optimum pH of 6.0, total biomass removal was determined to be 93% (1302 mg/L), lignin removal is 64%, PI and color reduction is 57% and 90%, respectively. Compared with the widely used polyaluminum chloride (PACl) coagulant, PEI is characterized by higher indices of the removal of total biomass and lignin, as well as color and PI at the application dose 2.8 times lower than that for the PACl.

Keywords: hydrothermal treatment; wastewater; biomass; coagulation.

1. Introduction

Biomass pre-treatment, directed to the destruction of the lignocellulosic matrix, occupies a leading position in lignocellulosic biorefinery for obtaining biofuels and chemicals from cellulose, hemicelluloses and lignin [1–3]. The production of veneer in Latvia and many countries of Eastern Europe is accomplished by the hydrothermal treatment of hardwood in special water basins for 16–18 h at a temperature of approximately 50°C and in a normal pressure circumstances [4]. Depending on the conditions of the hydrothermal treatment a different yield of wood hydrolysis products occurs due to the hydrolysis of the lignocellulosic matrix [5]. As a result, the formed effluents are polluted with lignin, hemicelluloses, extractives and degraded products from these wood substances which are responsible for the enhanced chemical oxygen demand and the intensive color of the wastewater. The chemical indexes of the effluents depend on many factors, namely, the wood species, temperature, pH, etc. Keeping in mind the volume of the polluted effluents formed annually and the zero waste policy for rational use of bioresources, it is very important to extract the formed biomass from the effluents efficiently to achieve more rational utilization than the dilution with pure water to maximum allowable concentrations and discharging to natural water basins. It is known that sewage sludge can be used successfully for soil improvement [6] and for producing building materials [7] and sorbents [8]. Besides, the effective removing of biomass from the wastewater will allow returning the purified wastewater in the basic technological cycle. The reagent method of pollutants' isolation based on the coagulation and flocculation of colloidal particles is widely used in wastewater treatment. The most known coagulants/flocculants are represented by multivalent inorganic metal salts (mainly aluminum and ferric

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sulphates and chlorides) and water soluble anionic and cationic polymers which can be used separately or in defined combinations [9–10].

The aim of the study was to evaluate the chemical composition of the biomass from birch wood hydrolysate imitating industrial wastewater and to determine the effectiveness of the isolation of wood biomass from this wastewater with polyethyleneimine (PEI) and compare it with the known and widely used inorganic coagulant.

2. Materials and methods

Hydrothermal treatment of 60 g of sawdust (< 1.00 mm) was performed with 0.04% NaOH solution at the hydromodulus 1/50 (mass ratio of the oven dry sawdust to water) and a temperature of 90°C for 4 h, using a 5 liter three-neck flask equipped with a return condenser, a thermometer and a stirrer. After hydrolysis the cooled hydrolysate was separated from the treated sawdust by filtration and the obtained biomass was dried to a constant mass, at first, at room temperature and then in an oven at 40°C. The treated sawdust was washed with distilled water to remove the adsorbed hydrolysed degraded products and dried to a constant mass, at first, at 60°C and then in an oven at 105°C. The characteristics of the treated sawdust and the obtained hydrolysate are represented by their average arithmetic values.

The elemental composition of the sawdust and was determined with the Elementar Analysensysteme GmbH (Germany). Inorganic matter (ash) was found according to Obolenskaya and co-authors [11]. The composition of birch sawdust – lignin, hemicelluloses, cellulose and extractives, before and after hydrolysis, was determined according to analytical chemical procedures. The content of lignin and cellulose was determined by Klason [12] and Kurschner-Hoffer's [13] methods, respectively. The content of hemicelluloses was determined as a difference between the content of holocellulose found by treatment with sodium chlorite and glacial acetic acid and cellulose. The content of extractives represented the sum of the content of the wood substances dissolved in acetone, using a Soxhlet extractor, and in boiled water (100°C) for 3 h [11]. The found content of cellulose, lignin, hemicelluloses and extractives in the birch wood residue was the following: 40.3%, 25.2%, 29.2% and 3.9%, respectively. Biomass component composition was identified by Fourier Transform Infrared (FTIR) and Ultraviolet-Visible (UV) spectroscopy. For FTIR- and UV-spectroscopy, a spectrophotometer (Perkin-Elmer Spectrum One, USA) with KBr tablets and a UV-VIS Spectrometer GenesysTM 10 (Thermo, USA) were employed.

Monosugars in the hemicelluloses fraction were determined by a high performance liquid chromatography (HPLC) using a liquid chromatograph (LC) SHIMADZU LC-20A (Shimadzu, Tokyo, Japan) with a refraction index detector. HPLC grade acetonitrile (Sigma-Aldrich, Germany) and water (distilled and deionised) was used for the HPLC analysis. Xylose, arabinose, rhamnose, mannose, glucose and galactose were reference standards. The column configuration was an Alltech Platinum Amino column (100Å 5u, 250×4.6 mm) with a Platinum Amino (NH₂) guard column (5u, 7.5×4.6 mm). The flow rate was 1.5 ml/min and the separation was performed at 35°C. The mobile phase consisted of a degassed filtered mixture of acetonitrile and water (80:20 %v/v). For measuring, a 1.0% biomass water solution in 0.01M NaOH was prepared and filtered through a 0.45 µm membrane filter before injection, filled in 1.5 ml bottles with caps and placed in an auto-injector. All samples were tested three times. Z potential of the hydrolysate was measured with Malvern Nanosizer SZ (UK). ¹³C-NMR spectrum of the dried biomass was recorded on a Bruker 300MHz spectrometer from 150 mg of the sample dissolved in 4% NaOD (1.0 mL).

Polyethyleneimine (PEI, molecular mass of 750 kDa) (Fluka) and polyaluminium chloride (PACl) (POLYPACS-30, China) (Al₂O₃ 30%, basicity 80–85%) was used for the treatment of the hydrolysate for biomass isolation by coagulation. All the coagulation experiments were conducted at a room temperature. The process of coagulation was done by mixing equal volumes of the coagulant and the hydrolysate. After the addition of the coagulant the pH value of the mixture was adjusted and it was stirred for a period of 1 min at 200 rpm followed by slow mixing at 40 rpm for 2 min. The effectiveness of coagulation was defined after system settling time of 120 min and filtration. The residual concentration of biomass and lignin was defined by measuring the obtained filtrate's optical density (*A*) at 490 and 280 nm using the previously obtained correlation curves for the biomass and lignin. Chemical oxygen demand (COD), color and permanganate index (PI) for the obtained hydrolysate were determined according to ISO 6060:1989, ISO 7887:1994 and ISO 8467:1993 standards. The efficiency of the model solution purification from total biomass, lignin, reduction of PI and color were calculated by using the following Eqn (1):

$$removal, \% = \left[\frac{(C_i - C_f)}{C_i} \right] * 100 \quad (1)$$

where C_i and C_f are initial and final concentrations of biomass, lignin, PI and the color.

3. Results and discussion

3.1. Hydrolysate and biomass characteristic

As shown in Table 1 below, the obtained hydrolysate was characterized by a moderate alkaline pH value, a low concentration of dry matter, representing the sum of wood degraded products passing to the hydrolysate, a moderate value

of chemical oxygen demand (COD) and a pronounced color associated with the presence of lignin and lignin-like substances in the hydrolysate.

Table 1. Parameters of the obtained hydrolysate

Sample	pH	Dry solids, g L ⁻¹	Density, kg m ⁻³	COD, mg O L ⁻¹	Colour, mg Pt L ⁻¹
Hydrolysate	9.02	1400	0.998	1285	746

The average yield of the solid biomass from the hydrolysate was $7.1 \pm 0.2\%$ relative to the initial sawdust mass. The yield calculated from the sawdust mass loss was a little higher than from the dried biomass which may be associated with a partial adsorption of the formed degraded wood products at the sawdust surface. 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. A SEM image (Fig. 1) characterized the obtained lignocellulosic biomass as an amorphous one without pronounced morphological features.

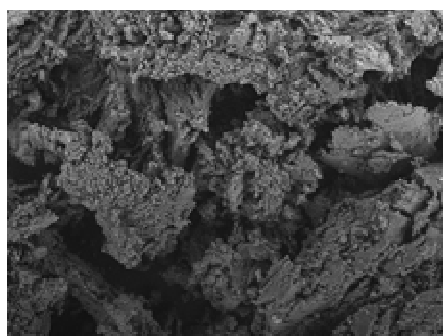


Fig. 1. SEM image of the biomass

The biomass had an enhanced ratio of O/C close to 1.5 ± 0.1 that indicated the presence of a substantial amount of oxygen-containing groups including hydroxyl, carbonyl and carboxyl groups in the hydrolysed wood products. The zeta potential value of the hydrolysate close to -30 mv testified the high content of these 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 lignin and hemicelluloses fragments.

For fuller characterisation of the chemical composition of the biomass, the FT-IR and UV spectroscopy were applied. The interpretation of the obtained results was based on the literature data concerning the studies of lignin and hemicelluloses by the methods [14–16].

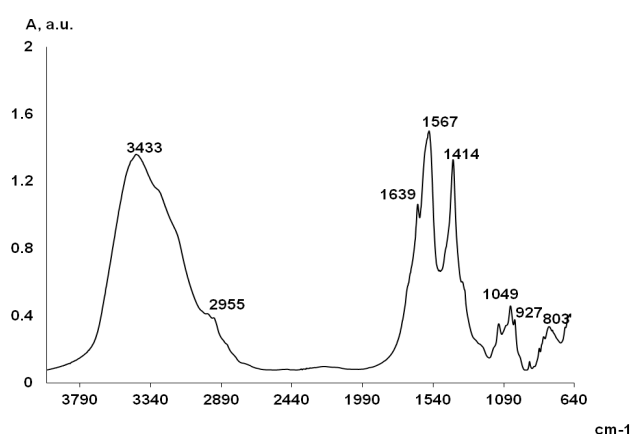


Fig. 2. FT-IR spectrum of the biomass

According to the FT-IR spectrum of the biomass (Fig. 2) the strong broad band at 3433 cm^{-1} is attributed to both aromatic and aliphatic hydroxyl groups. The band at 2955 cm^{-1} is caused by C–H stretch vibrations in the methoxyl, methyl and methylene groups present in the aromatic and saccharide structures of the hydrolysed products. The narrow bands at 1639 cm^{-1} and 1567 cm^{-1} may be assigned to the presence of ketones, carbonyls and ester groups in the biomass lignin and hemicelluloses. At the same time, in the spectrum, the pronounced bands corresponding to the aromatic skeletal vibrations of lignin structures, namely, 1600 cm^{-1} and 1505 cm^{-1} [17] are absent. The presence of lignin structures in the biomass is testified by the absorbance at 1414 cm^{-1} , assigned to skeletal vibrations and C=O group stretching in the syringyl and

guaiacyl aromatic rings. The CH_2 deformation vibrations appear at 1351 cm^{-1} and may be caused by both lignin and hemicelluloses structures. The bands in the region of $1115\text{--}803\text{ cm}^{-1}$ are typical for hemicelluloses. This region contains C-C ring vibrations, overlapped with the stretching vibrations of C-OH side groups and the C-O-C glucosidic band vibrations. The band at 1115 cm^{-1} may be caused by the presence of pectin. The band at 1047 cm^{-1} is attributed to the C-O-C stretching in glucosidic linkages, which is typical for xylan. The small bands at 927 cm^{-1} and 803 cm^{-1} are characteristic of the β -glucosidic bonds between the sugars units.

The obtained UV spectra testify the presence of aromatic fragments in the biomass, namely, the absorption at 280 nm is typical for lignin. At the same time, the relatively low value of the calculated extinction coefficient ($3.89\text{ l g}^{-1}\text{cm}^{-1}$) at this band indicates the dominant content of the non-aromatic structure in the dried biomass.

The chemical and morphological characteristics of the precipitated birch lignin were studied by Shulga and co-authors [18]. Hemicelluloses in the biomass were identified by a liquid chromatograph. The identifying HPLC analysis (Fig. 3) testified the presence of xylose, mannose, arabinose, rhamnose and glucose monomers in a 1.0% birch hydrolysate.

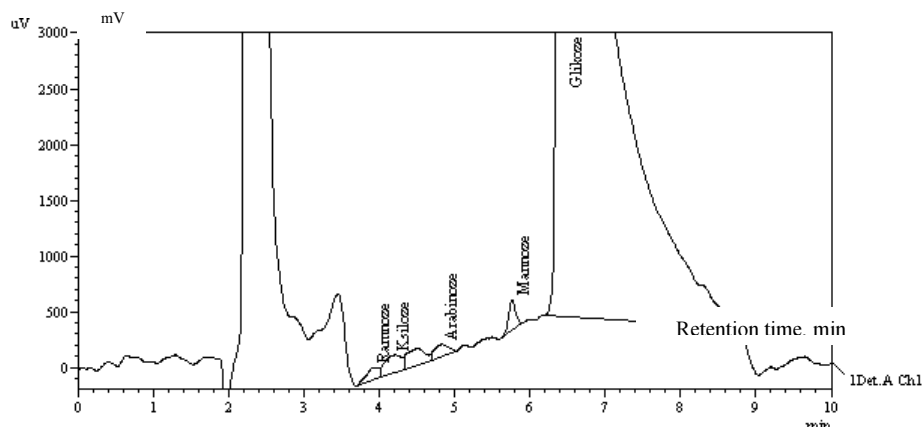


Fig. 3. HPLC chromatogram of a 1% biomass aqueous solution in 0.01M NaOH

The obtained quantitative data analysis indicated that the content of the first four sugars in the obtained hydrolysate was comparatively low and did not exceed 0.1%. This means that the hemicelluloses in the hydrolysate are represented mainly by polysaccharides. At the same time, the glucose content in the hydrolysate was higher and was close to 0.4%, which may be associated with the features of the birch lignocellulosic matrix degradation during the hydrolysis.

For obtaining more detailed information about hemicelluloses in the hydrolysate, the ^{13}C -NMR method was applied. The ^{13}C -NMR spectra (Fig. 4) demonstrates five pronounced signals at 102.3, 75.9, 73.7, 73.3 and 63.3 ppm, assigned to C-1, C-4, C-3, C-2 and C-5 of β -D-xylopyranoside units. The signal at 23.3 ppm may be assigned to carbon atoms in lignin methoxyl groups. The two signals observed at 56.02 and 168.4 ppm may be assigned to methoxyl groups in the lignins' aromatic rings and the carboxyl group of glucuronic acid, respectively. The signals at 74.8–75.9 ppm may be assigned to C3 in β -D-glucose and C5 in β -mannose. The shift at 118.7–119.7 ppm can be attributed to the presence of an ester bond between the carboxyl group of D-glucuronic acid and phenylpropan side chains of lignin. The signal at 129.4 ppm may be assigned to carbon atoms in the p-substituted lignin aromatic ring.

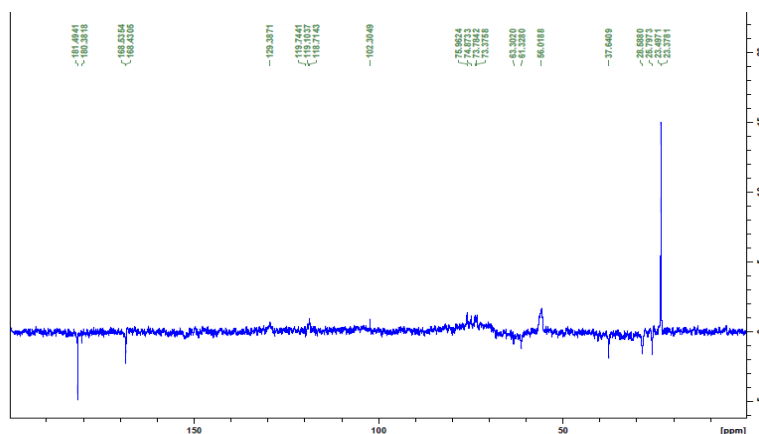


Fig. 4. ^{13}C CMR spectrum of the dried biomass

To fractionate the lignocellulosic biomass and calculate the content of lignin and hemicelluloses therein, the precipitation of the hydrolysate with concentrated sulphuric acid with the following treatment of the formed filtrate with ethanol according to Liu and co-authors [19] was employed. The scheme of the applied fractionation is given in Fig. 5.

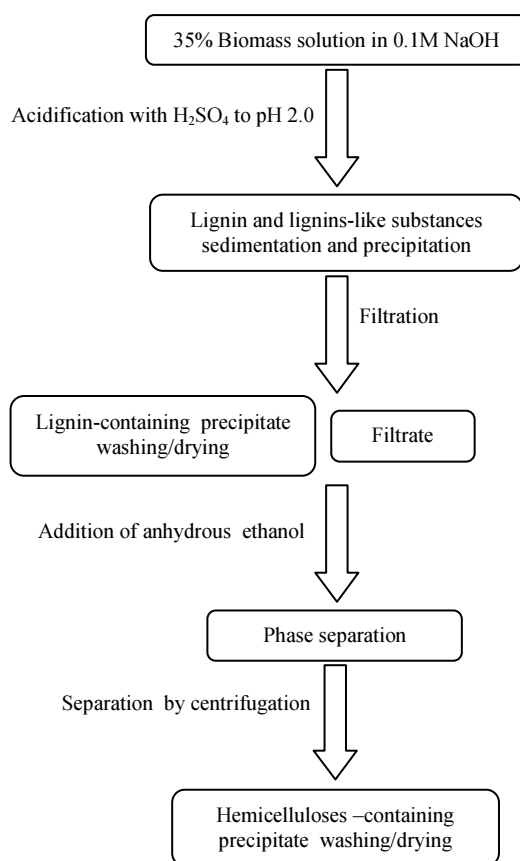


Fig. 5. Scheme of biomass fractionation

For the fractionation the biomass dried at room temperature was dissolved in 0.1M NaOH for obtaining 50 ml of a 35% biomass solution. The concentrated hydrolysate was, at first, acidified with 20% sulphuric acid to a pH of 2.0 at room temperature with the following filtration and centrifugation of the obtained suspension for separating the lignin-containing fraction. The lignin precipitate was washed with distilled water to pH 5.5 and dried in an oven at 40°C. Anhydrous ethanol was added to the obtained filtrate at the volumetric ratio of ethanol/filtrate close to 4. After addition of anhydrous ethanol, the hemicelluloses-containing fraction precipitated and then was isolated by centrifugation, washed with the ethanol and dried in an oven at 40°C. The content of hemicelluloses- and lignin-containing fractions in the biomass was assessed from the masses of the obtained dried precipitates.

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. At the same time, the low molecular products of the lignocellulosic matrix destruction that were not able to be precipitated by this procedure occupied 11.3% of the solid biomass. The measuring of the content of water-soluble lignin [11] in the filtrate obtained after the Klason lignin [12] extraction corresponded to 5.89%, and the total content of lignin (Klason and water-soluble) in the biomass was 10.9%. As the obtained results have shown, the content of lignin, hemicelluloses and water-soluble degraded wood products in the solid biomass corresponded to the following mass ratio: 1.2/6.7/1.0, respectively.

Table 2. Wood component composition of birch sawdust before and after the hydrolysis

Sample	Holocellulose, %	Cellulose, %	Hemicellulose %	Lignin, %
Untreated	68.5	40.3	28.2	25.2
Treated	70.4	46.8	23.6	25.1

Simultaneously, the changes in the wood composition of birch sawdust due to its hydrolysis were assessed. According to the results listed in Table 2 the main changes in the wood composition caused by the hydrolysis took place for cellulose, i.e., its content increased by 6.5% and hemicelluloses, i.e., their content decreased by 5.6%, while the content of lignin diminished by only 0.1%. It is reasonable to assume that the gain in the cellulose content and the negligible alteration in the lignin content in the pre-treated lignocellulosic matrix were associated with the notable losses of hemicelluloses and water-soluble extractives during the hydrothermal treatment.

3.2. Isolation of the biomass by coagulation

Polyethyleneimine (PEI) was selected as a coagulant for isolation of the biomass from model woodworking wastewater. Polyethyleneimines are highly branched polymers with primary, secondary and tertiary amine groups which behave like cationic polyelectrolytes because the amine groups are partially protonated in acidic and neutral pH conditions.

In coagulation–flocculation processes, coagulant dosage and pH plays an important role in determining the coagulation efficiency. Optimal conditions of biomass coagulation from the hydrolysate were searched in a PEI dosage range of 7–140 mg/l and in a pH interval of 3–10. Figure 6 clearly indicates that PEI coagulation efficiency highly depends on pH and dosage. Total biomass and lignin removal and PI reduction efficiencies increase with increase in coagulant dosage and pH until it reaches its highest value, optimum pH, after which the removal and reduction efficiencies start to decrease. The optimum dosage is 35 mg/L and the optimum pH is approximately 6.0. At the optimum PEI dosage and pH up to 93% (1302 mg/L) of total biomass, 64% of lignin, 90% of color and 57% of PI was reduced.

For comparison one of the most widely used inorganic coagulant polyaluminium chloride (PACl) was selected. PACl and its analogues are considered to be the most effective coagulants in high color wastewater treatment [20–21]. It was determined that the optimum PACl dosage and pH are 100 mg/L and 6.0, respectively. This result reveals that the optimum coagulant dosage for PEI is 2.8 times lower than that of PACl but the optimum pH for both coagulants remains the same at pH 6.0. The extraction of the total biomass with PACl is 80%, and that of lignin is 53% while these values for PEI are higher, namely, 93% and 64% (Fig. 7). PEI is characterised by higher indices of the removal of total biomass and lignin, as well as color and PI at the lower application dose than that for the PACl.

The higher efficiency of the PEI as a coagulant may be governed by realising the hybrid mechanism of the biomass components' precipitation which includes their coagulation, following the pattern of charge neutralisation, and its flocculation, following the pattern of bridge formation, taking into account its high molecular mass, in contrast to PACl, which precipitates the biomass mainly according to the heterocoagulation mechanism. This is favoured by the high density of the charge of PEI macromolecules, its branching, and the high molecular mass. At the same time, the moderate values of a PI reduction for both PEI and PACl may indicate the presence of an essential content of low-molecular products of the hydrolysed lignocellulose that are not possible to extract with these coagulants, and additional post-treatment of the hydrolysate after its coagulation is needed.

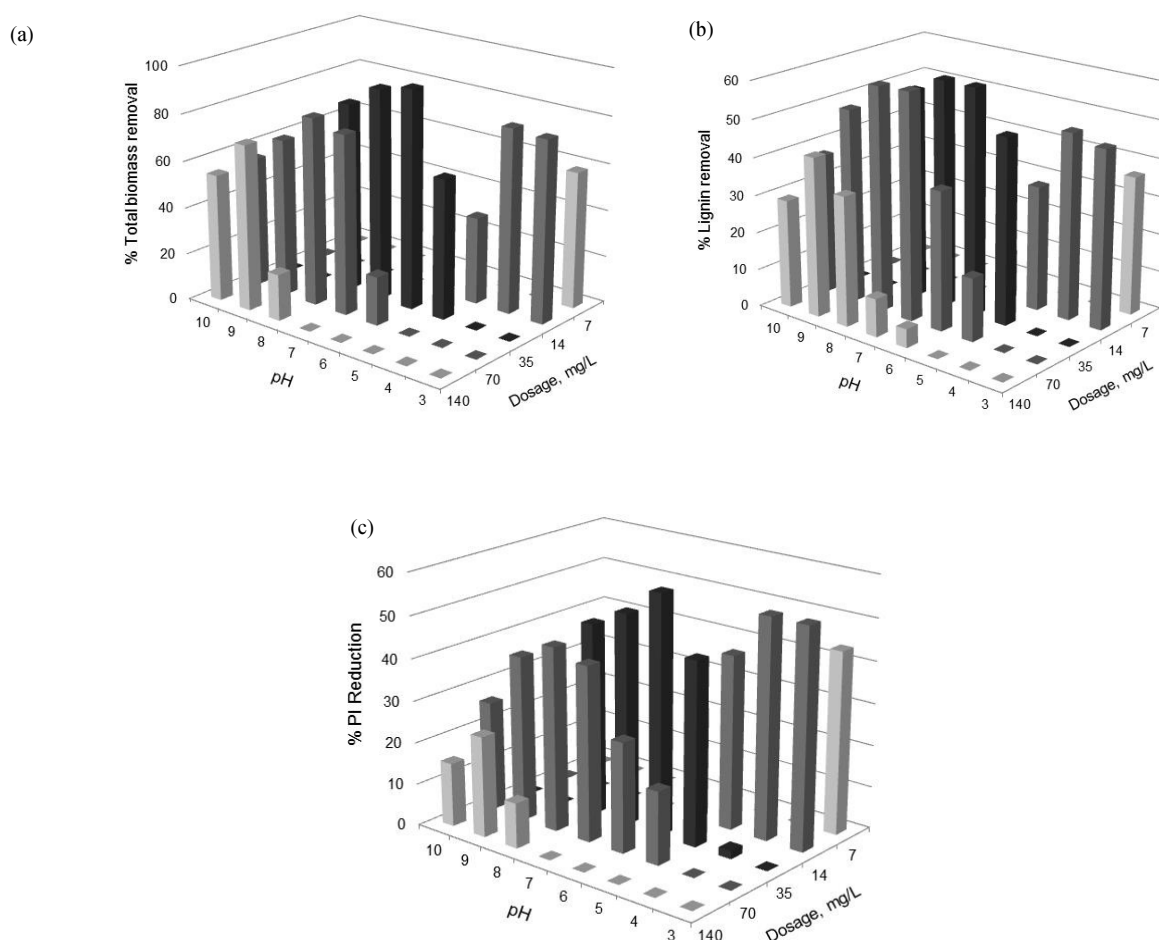


Fig. 6. Effects of PEI dosage and pH on (a) total biomass removal, (b) lignin removal and (c) PI reduction

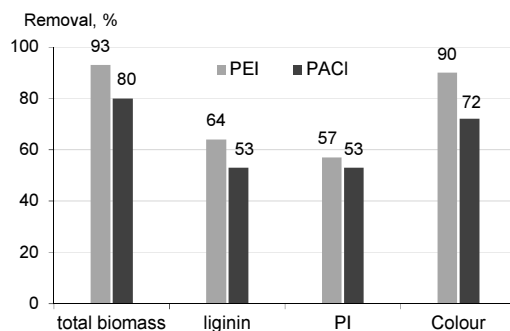


Fig. 7. Comparison of total biomass, lignin, PI and colour removal for PEI and PACI at optimal coagulant dosage and pH

4. Conclusion

For imitating woodworking wastewater, birch sawdust was hydrothermally treated in mild alkaline conditions at 90°C. The yield of the solid biomass did not exceed 7% and contained mainly hemicelluloses in the polysaccharide form and lignin. The applied instrumental analysis (FTIR-, UV- spectroscopy) testify the dominant content of hemicelluloses in the obtained biomass. The study of the biomass with a high performance liquid chromatograph identified, along with xylose, glucose and mannose, also arabinose and rhamnose. The fractionation of the biomass was performed using concentrated sulphuric acid and ethanol. As the obtained results have shown, the content of lignin, hemicelluloses and water-soluble degraded wood products in the solid biomass corresponded to the following mass ratio: 1.2 /6.7/1.0, respectively.

PEI is characterized by higher indices of the removal of total biomass (93%, 1302 mg/L) and lignin (64%), as well as color (90%) and PI (57%), at the application dose 2.8 times lower than that for PACI. The higher efficiency of PEI as a precipitant may be governed by realizing the hybrid mechanism of the biomass extraction which includes its coagulation following the pattern of charge neutralization and its flocculation following the pattern of bridge formation in contrast to PACI, precipitating biomass mainly according to the heterocoagulation mechanism. This is favored by the high density of the charge of PEI macromolecules, its branching, and the high molecular mass.

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