

# **Difference in the treatment effectiveness of woodworking wastewater between polyaluminium chloride-based coagulants**

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**Abstract.** In the work, a comparative study of the efficiency of coagulation of a model solution, simulating woodworking wastewater, with the known composition of polyaluminium chloride (PAC) with aluminium sulphate and a new PAC-based composite coagulant was carried out. It has been found that, in comparison with the known composition, the developed composite coagulant makes it possible to enhance the efficiency of the wastewater treatment and to decrease the content of residual aluminium therein, which enables the return of the treated water in the technological cycle. The enhancement of the coagulation ability of the developed composite coagulant relative to the known composition of PAC with aluminium sulphate is governed by the formation, in the AlCl<sub>3</sub>/PAC system, of polynuclear Al-complexes with a high-molecular structure. This is testified by the results of the comparative study of those coagulants by the Ferron and ion mass spectroscopy methods.

**Keywords:** coagulation, composite coagulants, polyaluminium chloride, wood hydrothermal treatment, model wastewater, hemicelluloses and lignin containing pollutants.

## I INTRODUCTION

The qualitative and quantitative treatment of woodworking wastewater makes it possible to return the purified water into the technological cycle, which is important from both economic and ecological viewpoints. It is known that aluminium salts – aluminium sulphate and aluminium chloride, and polyaluminium chloride have found wide application as a coagulant [1, 2].

According to Chernoberezhsky [3, 4], aluminium sulphate, at a content of no more than 150 mg/L in wastewater, quantitatively removes lignin in acidic media with a pH of 4.5-5.0. In its turn, aluminium chloride is most effective at pH 6.0 and the dosage 100-110 mg/L [5, 6]. It should be mentioned that the decrease of the wastewater temperature from 22°C to 2°C has an adverse effect on the coagulation ability of aluminium salts, namely, the optimum dosage of aluminium sulphate and chloride as well as the optimum coagulation time increase several times [7].

It is known [8, 9] that polyaluminium chloride (PAC) is a more efficient coagulant than aluminium sulphate and chloride. It has been found [10] that, for 91% of the decrease in COD of the pulp industry wastewater, the required dosages of aluminium sulphate and PAC are 1000 mg/L and 500 mg/L,

respectively. It is shown [11] that, for treating the pulp industry wastewater with a high pollution load (COD 7000 mg/L), the optimum value of pH is 4.0, but the required dosages of aluminium chloride and PAC grow up to 5000 mg/L and 2400 mg/L, respectively. It has been established [12] that the optimum pH for PAC and aluminium chloride is equal to 6.0. However, at this value of pH, the concentration of organic substances in the treated wastewaters, representing water-soluble complexes with aluminium ions, is higher for chloride aluminium than for PAC. This is the reason for the enhanced content of residual aluminium in wastewater. As shown in the studies on the coagulation of wastewater [13, 14], polluted with compounds of wood origin, the optimum dosage of PAC does not exceed 100 mg/L. At the same time, according to our results [15, 16], PAC as a coagulant is characterized by a weaker ability to purify woodworking wastewater than the high molecular polyethylenimine.

To enhance the efficiency of the coagulation ability, PAC are used in compositions with different chemical reagents, for example, calcium oxide and chloride [17, 18], iron oxides or halogenides [19, 20], natural bischofite [21, 22], silicic acid and iron [23]. The use of PAC with a cation copolymer of acrylamide and

dimethylaminoethylmethacrylate [24], with a cation flocculate based on polyacrylamide, is also known [25]. There are also a range of methods for effective treatment of wastewaters, including their stage-by-stage treatment, firstly, with aluminium sulphate and then with polyaluminium chloride [26, 27]. However, such a mode is complicated from the technological viewpoint due to the multistageness of the coagulation process.

The aim of the present work was to compare the efficiency of the coagulation ability of the known composite coagulant and the PAC-based coagulant developed by us. The main criteria of efficiency were the residual concentration of pollutants, the concentration of residual aluminium in wastewater, and the colour degree of wastewater after its treatment in a temperature range of 14-40°C.

## II MATERIALS AND METHODS

In the study, polyaluminium chloride Polypacs-30 (basicity ~ 80%, mass fraction of  $\text{Al}_2\text{O}_3$  ~35%) was used. For comparison purposes, the new composite coagulant developed by us [28], representing a complex compound of PAC and aluminium chloride, and the known coagulant, incorporating PAC and aluminium sulphate [29], were used. The mass ratio of the reagents in the new coagulant varied from 1/1 to 10/1 (PAC/ $\text{AlCl}_3$ ), while the mass ratio of  $\text{Al}_2(\text{SO}_4)_3$  and PAC varied in the range of 2.7/1-0.5/1 (PAC/ $\text{Al}_2(\text{SO}_4)_3$ ). The applied dosage of coagulants varied from 50 to 150 mg/L. As aluminium salts,  $\text{AlCl}_3 \cdot \text{H}_2\text{O}$  and  $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$  were used.

The developed and known aluminium coagulants have been described by the traditional Ferron method [30] and by electrospray ionization (ESI) mass spectrometry [31]. Al (III) reacts with a Ferron reagent to form an Al-Ferron complex at pH 5.0,  $\lambda_{\text{max}} = 370 \text{ nm}$ . A Genesys(TM)10 spectrophotometer was used to measure the Al-Ferron kinetics. The absorbance at 370 nm was recorded from 30 s to 7200 s. Therefore, based on detecting the mass to charge ratio ( $m/z$ ) of complexes, the ESI-MS measurement proved to be a good method for aluminium speciation. To investigate aluminium hydrolysis of the coagulant at pH 6.0, the coagulant was diluted to a concentration of  $1.5 \cdot 10^{-4} \text{ mol L}^{-1}$ . The ESI mass spectra were recorded with a micromass hybrid quadrupole time of a flight mass spectrometer (GCMS-QP2010) equipped with an electrospray ion source. The solutions were introduced into the spectrometer at a flow rate of  $10 \mu\text{L min}^{-1}$ . The instrumental conditions were as follows: capillary voltage 3500 V, sample cone voltage 70 V, source temperature 120°C, cone gas ( $\text{N}_2$ ) flow rate  $300 \text{ L h}^{-1}$ , and mass range 60-600.

The wastewater of a woodworking enterprise was simulated with a model solution, obtained by way of

hydrolysis of birch sawdust according to [14]. The mass ratio between the sawdust and the liquid phase was 1:50. Hydrolysis was carried out at a temperature of 90°C during 6 h 20 min, from which, within 40-50 min, the required temperature was reached; the cooking process at 90°C proceeded for 4 h and then the system cooled during 1.5 h. To obtain model wastewater, the obtained solution was filtered for removal of fine-disperse particles. The physical parameters of the model solution are listed in Table 1.

TABLE 1  
Characteristics of the model wastewater

Parameters	Value
Hemicelluloses, lignin and wood extractive substances (HLES)	1400 mg L <sup>-1</sup>
Lignin-originated substances (LSV)	280 mg L <sup>-1</sup>
Chemical Oxygen Demand (COD)	1285 mgO L <sup>-1</sup>
Colour	746 mg L <sup>-1</sup> Pt <sup>-1</sup>
Total Organic Compounds (TOC)	732 mg L <sup>-1</sup>
pH	9.02
Kinematic Viscosity	3.81 mPa s <sup>-1</sup>

The elemental and functional composition of the dry matter of the model solution is presented in Table 2.

TABLE 2  
Elemental and functional composition of the dried solid from the model wastewater

C, %	37.70
H, %	4.70
O, %	57.16
S, %	0.14
N, %	0.30
OCH <sub>3</sub> , %	2.29
CO, %	1.15
OH, %	10.15

A study of the component composition [32] showed that the dry matter of the model solution consisted of 75-80% of hemicellulose compounds (HCC), which were isolated from the model solution by ethyl alcohol according to the known procedure [33]. The content of the formed Klason lignin in the residue formed did not exceed 10%.

The coagulation process was carried out by way of mixing the model solution and the solution of the composite coagulant at a ratio of 1:1. The composite coagulant solution was introduced into the model solution, at a constant mixing with a rate of 100 r.p.m. After 1-min stirring, a certain amount of HCl was introduced into the system so that to reach the required pH value (4.0-9.0). After reaching the pH, stirring was continued at a rate of 200 r.p.m. during 1 min, and then at a rate of 40 r.p.m. during 2 min.

Experiments were conducted in the temperature range of 14-40°C. Coagulation at low temperature was carried out by way of mixing the model solution and the solution of the composite coagulant with a temperature of 14(±1)°C, which was reached by way of cooling the solution in a thermostat (MLW U7<sup>c</sup>) using tap water. Similarly, the lowered temperature was maintained during 2 h of the coagulation process. For the coagulation at a temperature of 40°C, the model solution, pre-heated up to 60 (±1)°C, and a solution of the composite coagulant with a temperature of 20 (±1)°C were used. As a result, the coagulation temperature was 40 (±1)°C, which was maintained in the coagulation process by way of using a Julabo thermostat.

The efficiency of the coagulation was defined after 2 h of the system's settling and filtration. UV/Vis spectrophotometer Genesys 10UV was used to measure the optical density of the effluent at wavelengths of 490 nm and 280 nm. These wavelengths correspond to the different chemical composition of wastewater: 490 nm corresponds to the removal of HLES and 280 nm is related to the removal of lignin compounds, which are usually present in the wastewater. Colour (LVS EN ISO 7887:1994), COD (LVS EN ISO 6060:1989), TOC (LVS EN ISO 1484:2000) and residual aluminium (GOST 18165-89) were determined according to standard methods

Coagulation efficiency was determined, comparing the initial parameters of the model solution with the parameters obtained for the filtrate after coagulation, using the following formula:

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

where  $C_i$  and  $C_f$  are the initial and final concentrations of HLES, LSV, COD and the colour.

### III RESULTS AND DISCUSSION

At first, the effect of temperature on the efficiency of HLES coagulation with the new and known composition coagulants was studied. Fig. 1 (a, b) shows the results of the comparison of the treatment effectiveness of the model solution at pH 6.0 and the application dosage of composite coagulants equal to 100 mg/L at different treatment temperatures.

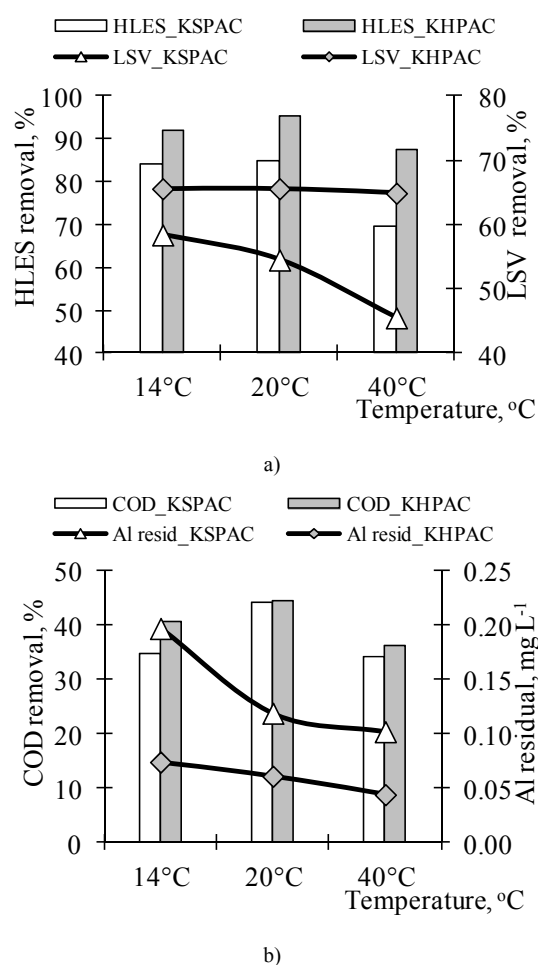


Fig. 1. HLES and LSV removal (a), COD removal and residual aluminium (b) of the model wastewater after coagulation using 100 mg L<sup>-1</sup> composite coagulants at pH 6.0 depending on temperature.

The obtained results show that the new composite coagulant AlCl<sub>3</sub>/PAC, at the components' mass ratio of 1/1, is characterized by a higher degree of purification of the model solution from HLC and LC in the whole temperature range. The highest efficiency of the model solution is reached upon the use of AlCl<sub>3</sub>/PAC with a ratio of 1:1 at a temperature of 20°C; in this case, the removal of HLC and LC is 95.3% and 65.6%, respectively. COD and colour decrease by 44.4% and 88.0%, respectively, and the residual concentration of aluminium is 0.061 mg/L. A comparison of the quality of treating the model solution using AlCl<sub>3</sub>/PAC with a ratio of 1:1 relative to Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>/PAC of the composition 2.7/1 shows that, at a temperature of 14°C, the removal of HLC and LC increases by 8% and 7%, respectively, while that of COD decreases by 6%; in this case, the content of residual aluminium in the model solution falls 2.5-fold. At a temperature of 20°C, the removal of HLC and LC increases by 11% and 10%, respectively, but the decline in COD grows by 2%. In this case, the content of residual aluminium in the treated model

solution decreases twice. With increasing temperature up to 40°C in the model solution, treated with the new composite coagulant, the increment in the removal of HLC, LC and COD grows up to 18%, 21% and 4%, respectively, while the content of the residual aluminium decreases 2.3-fold, in comparison with the solution treated with the known coagulant.

Since the coagulation process is rather sensitive to decreased temperatures, it was of interest to compare the coagulation efficiency of the composite coagulants at temperatures below 20°C. Table 2 lists the results of the treatment of the model solution depending on the medium pH at a temperature of 14°C and the dosage of the applied coagulants 100 mg/L.

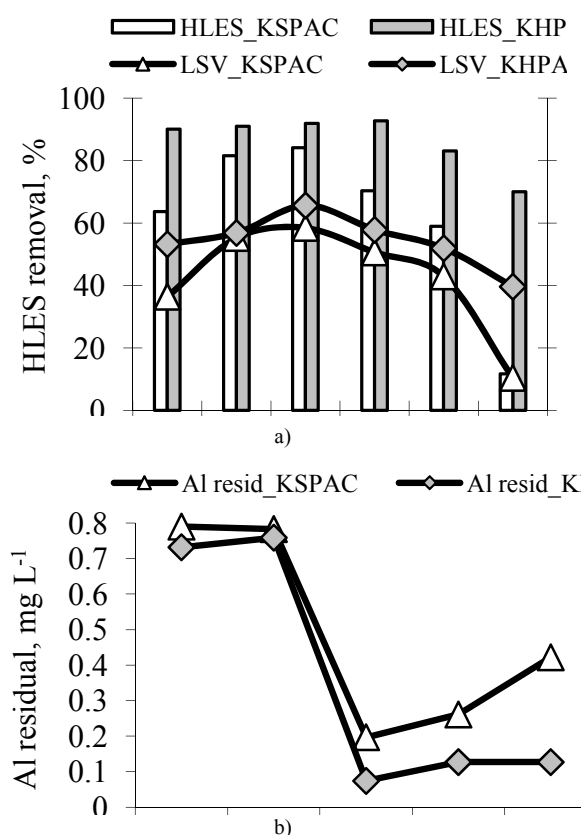


Fig. 2. HLES and LSV removal (a) and residual aluminium of the treated model wastewater (b) after coagulation using 100 mg L<sup>-1</sup> composite coagulants at a temperature of 14°C depending on pH.

The obtained results show that the new composite coagulant is characterized by a higher degree of purification of the model solution from HLC and LC, in comparison with the new coagulant, in the whole pH range. The maximum effectiveness of treatment is in the pH range of 5.0-7.0. At the same time, the elevated value of the residual concentration of aluminium in the model solution (0.074-0.127 mg/L) at pH 5.0 after its treatment is not desirable from the viewpoint of the return of the treated water in the technological cycle. Therefore, the recommended pH values for purifying wastewaters from HLC and LC at

lowered temperatures vary in the range of 6.0-7.0. At one and the same application dosage, the enhancement in the coagulation pH from 5 to 6 increases the removal of HLC and LC up to 8% and 7%, respectively; in this case the content of residual aluminium in the model solution decreases down to 2.5 times. The further increase in the pH value up to 7.0 increases the removal of HLC and LC by 22% and 7%, respectively, while the content of residual aluminium in the model solution decreases twice, in comparison with the same indices at pH 5. It should be mentioned that the developed composite coagulant demonstrates also the incomparably high coagulation efficiency in comparison with the known coagulant at pH values of 4.0 and 8.0. In weak acidic medium, the content of the model solution, using AlCl<sub>3</sub>/PAC with the ratio of 1/1, is more than 3-fold lower, compared with the case of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>/PAC with the ratio of 2.7/1. However, both the acidic and alkaline values of pH can have an adverse effect on the quality of the technological water.

The results of the study of the dosage of the composite coagulants on the treatment effectiveness of the model solution at pH 6.0 and a temperature of 14°C are shown in Figure 3.

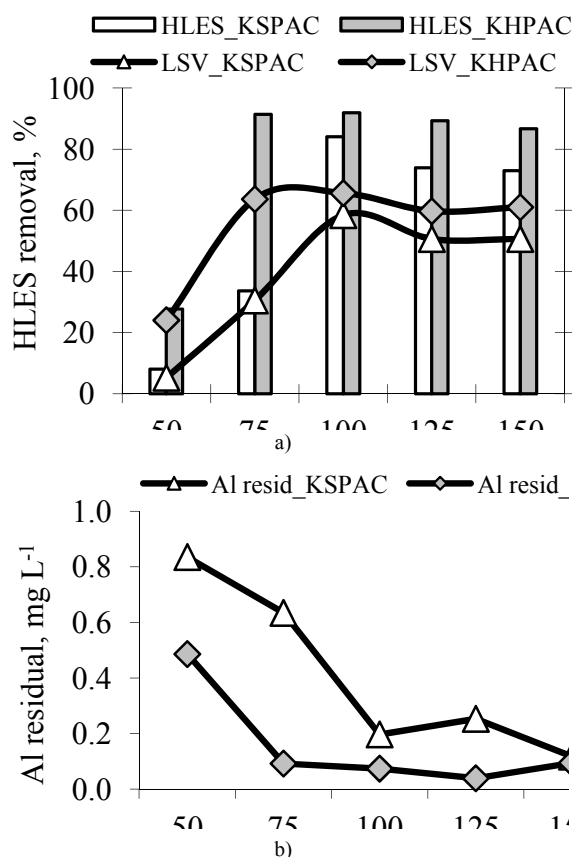


Fig. 3. HLES and LSV removal (a) and residual aluminium of the treated model wastewater (b) after coagulation using composite coagulants at a temperature of 14°C and pH 6.0 depending on the dosage.

A comparative analysis of the obtained results shows that, in the whole range of dosages, the new composite coagulant  $AlCl_3/PAC$  with the ratio of 1/1 demonstrates a higher degree of purification of the model solution from HLC and LC than the composite coagulant  $Al_2(SO_4)_3/PAC$  with the ratio of 2.7/1. In this case, the model solution is characterized by a much lower concentration of the residual aluminium after coagulation. The best results are reached in the dosage range of 75-125 mg/L. The efficiency of the removal of HLC, LC and COD, on the average, reaches 91%, 65% and 47%, respectively; colour – 90%, and residual concentration of aluminium – 0.04-0.09 mg/L. A comparison of the quality of the treatment of the model solution using the known coagulant at the application dosage of 75 mg/L has shown that the increase in the removal of HLC and LSV is 58% and 33%, respectively, while the content of residual aluminium in the model solution declines 8-fold. At the application dosage of 125 mg/L, the increase in the removal of HLC and LSV is 15% and 9%, respectively, while the content of residual aluminium declines 6.5-fold. A similar regularity is retained also upon the treatment of the model solution at pH 7.0. It is found that the model solution, after applying the new composition coagulant  $AlCl_3/PAC$  at the mass ratio of the components 1:1, pH 6.0 and the application dosage 100 mg/L, is characterized by the following indices: HLC – 33 mg/L, COD – 367 mg/L, colour – 60 mg/L Pt, TOC – 123 mg/L, residual aluminium – 0.061 mg/L.

We have found that the increase in the coagulation ability of the composite coagulant relative to the known coagulant is governed by the formation of polynuclear Al-complexes, having mainly the polymer and high-molecular structure in the  $AlCl_3/PAC$  system. This is confirmed by the results of the comparative study of the composite coagulants by the Ferron and ion mass-spectroscopy methods. The first method is based on the kinetics of the interaction of monomer, polymer and high polymer forms of aluminium with the Ferron reactive [30]. According to the obtained results listed in Table 3, the amount of the Al-containing polynuclear complexes, having a polymer and high polymer form, in the developed coagulant is greater than that in both the initial PAC and the  $Al_2(SO_4)_3/PAC$  system.

TABLE 3  
Contents of aluminium species in solutions of PAC-based coagulants

Coagulant	Al <sub>a</sub> , %	Al <sub>b</sub> , %	Al <sub>c</sub> , %
PAC	16.6	66.6	16.8
KSPAC	16.4	67.2	16.4
KHPAC	10.3	72.0	17.1

The second method of comparison is based on the qualitative analysis of the forms of the products of hydrolysis of composite coagulants by the ion mass-spectroscopy on a GCMS-QP2010 device (Shimadzu, Japan) [34]. The analysis of the aluminium forms was performed by the characteristic peaks with the intensity no less than 20%. The obtained spectra of PAC and composite coagulants are given in Fig. 4.

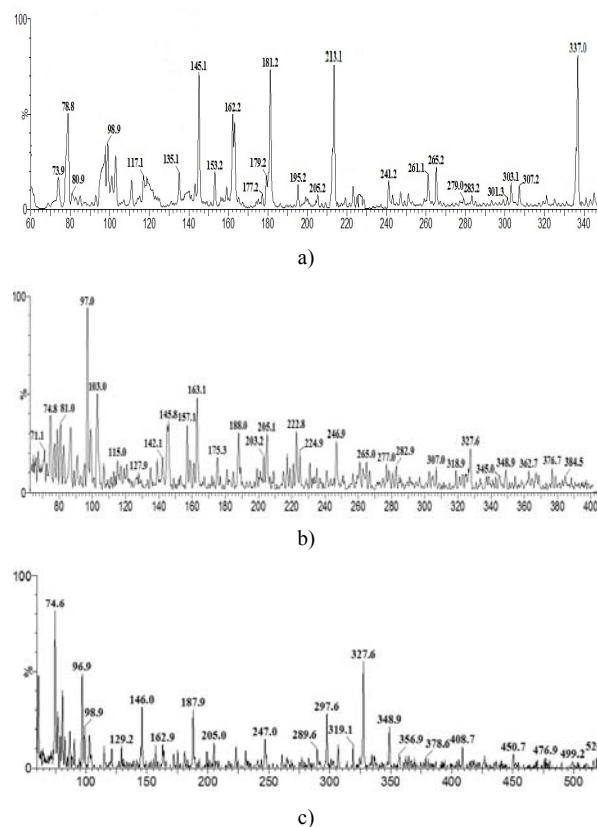


Fig. 4. ESI-MS spectra of the solutions of PAC (a), KSPAC (b) and KHPAC (c).

The PAC spectrum (Fig. 4, a) is characterized by signals of the monomeric forms of aluminium at 78.8 and 98.9  $m/z$ , and trimeric forms  $[Al_3O_4(H_2O)_{0.5}]^+$  at 145.1, 162.2, 181.2  $m/z$ . In turn, the intensive peaks at 231.1 and 337.0  $m/z$  correspond to the high molecular forms  $[Al_{13}O_{18}(H_2O)_{0.2.4}]^{3+}$  and  $[Al_{13}O_{18}(OH)(H_2O)_{0.4}]^{2+}$ , respectively. The composite coagulant  $Al_2(SO_4)_3/PAC$  (Fig. 1(b)), is characterized by signals of monomeric  $[Al(OH)_2(H_2O)_{1.2}]^+$  - 97.0  $m/z$ , dimeric  $[Al_2O_2(OH)(H_2O)_{0.4}]^+$  - 103.0, 157.1  $m/z$ , trimeric  $[Al_3O_4(H_2O)_{0.5}]^+$  - 145.8, 163.1  $m/z$ , tetrameric  $[Al_4O_5(OH)(H_2O)_{1.5}]^+$  - 188.0, 205.1, 222.8  $m/z$  and pentameric  $[Al_5O_7]^+$  - 246.9  $m/z$  forms of aluminium. The less intensive peak at 327.6  $m/z$  is characterized by the presence of the high polymer form of aluminium  $[Al_{13}O_{18}(OH)(H_2O)_{0.4}]^{2+}$ . In turn, for the developed composite coagulant  $AlCl_3/PAC$  (Fig. 4(c)), besides the presence of the above-mentioned

monomeric and polymeric forms of aluminium, the presence of the high molecular forms of the type  $Al_{12}O_{17}]^{2+}$  - 297.6 *m/z*,  $[Al_{13}O_{18}(OH)(H_2O)_{0-4}]^{2+}$  - 327.6 *m/z* and  $[Al_{14}O_{20}(H_2O)_{0-1}]^{2+}$  - 348.9 *m/z* is pronounced. The presence of peaks in the range of 400-550 *m/z*, which is characteristic for the high polymer forms of aluminium with 9, 10 and 16 atoms of aluminium in the structure, is observed [30, 34]. According to the present results, the composite coagulant  $AlCl_3/PAC$  is characterized by great amount and variety of the high polymer forms of aluminium.

#### IV CONCLUSION

The results of the treatment of the model solution, simulating woodworking wastewater, show that the use of the new composite coagulant based on chloride polyaluminium enables a considerable enhancement of the degree of treatment of the model solution from hemicelluloses and lignin compounds, in comparison with the new composite coagulant. The developed composite coagulant is efficient at both low and elevated temperatures, and is characterized by a minimum residual concentration of aluminium, which makes it possible to return the treated wastewater into the technological cycle.

#### V ACKNOWLEDGMENTS

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