ISSN 1691-5402
Environment. Technology. Resources
Proceedings of the 9th International Scientific and Practical Conference. Volume 1


# Characteristics of the Coagulate Obtained During the Process of Model Wastewater Treatment

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***Abstract.*** **In the process of wastewater treatment by coagulation a large amount of sediment is being produced, which is the main drawback of this method. Therefore, the development of utilization or recirculation technology of the waste obtained, the research of the obtained by-products should be conducted. Within the scope of this work, the sediment, that is being formed during the coagulation of the model wastewater containing the wood originated pollutants, was studied. Using the aluminium-containing composition coagulant on a base of polyaluminium chloride, coagulates characterized by the low sludge volume index within 30 minutes (89 ml $g^{-1}$), and the optimal time of sedimentation is 20-30 minutes. The coagulate particles have an average size of 45.8 µm. The derived coagulate is composed primarily of carbon (27.9%), oxygen (49.4%) and aluminum (10.9%). Carbon, oxygen and hydrogen belong to an organic part of coagulate - the wood pollutants, which, in turn, has a high content of hemicellulose. It is concluded that the existing hemicellulose in the obtained coagulate is characterized by O-acetyl-4-O-methyl-D-glucuron-β-D-xylan with β-(1-4)-glucomannose.**

***Keywords*** **– coagulation, model wastewater, coagulate, hemicellulose, lignin-containing substances.**

## I Introduction

Latvia is one of the major plywood manufacturers in Eastern Europe. The hydrothermal wood treatment is one of the stages of plywood production, resulting in water pollution by components such as hemicellulose, lignin and wood extractive substances (HLES). The wastewater can cause considerable damage to the receiving waters if discharged untreated.

Several physico-chemical colour removal methods such as rapid sand filtration, membrane processes and adsorption have also been developed [1, 2]. However, the most acceptable technology of wastewater treatment within the framework of enterprise, applied presently, is based on the processes of coagulation. Chemical coagulation is a frequently applied process in primary purification of industrial wastewater. Coagulation is mainly induced by inorganic metal salts, such as aluminium sulphates and chlorides [3]. Research and practical applications have shown that coagulation will lower the pollution load and could generate an adequate water recovery [4, 5].

However, it should be noted that the most important drawback of the coagulation method is the large amount of the produced sludge that needs to be eliminated or used as a raw material for other technologies. The sludge produced during the physical-chemical treatment has arisen due to the amount of organic matter and total solids in suspension that have been removed, and the compounds, formed from the coagulant applied. Sewage sludge can be used as a fuel with a high calorific value [6], as a component of soil recovery [7], for the production of building [8] and sorbent materials [9, 10].

Based on the above, the goal of the present study was to describe HLES coagulate, which occurs due to the process of model wastewater coagulation by using new Al-composition coagulants.

## II Materials and methods

The birch wood sawdust was used for the wood hydrothermal treatment. A hydrolysis was fulfilled in an alkaline water environment, at the water duty of 1/50, the temperature 90 °C and the duration was about 4 hours. The model wastewater was described by HLES content, COD, $BOD_5$ and its color [11, 12].

In order to find the wood pollutants coagulation pattern and to develop optimal conditions of wastewater treatment technologies, studies of the process of coagulation of model wastewater were completed using the aluminium-containing coagulants. The model wastewater coagulation process was performed using composite coagulant on PAC basis (COMPAC) [13] with dosage 100 mg $L^{-1}$ at pH 6.0 and a room temperature.

The coagulation tests involved the rapid addition of the coagulant to the model wastewater followed by stirring at 100 rpm. After addition of coagulants, the model wastewater was stirred for a period of 1 min at 200 rpm and then it was followed by a further slow mixing of 2 min at 40 rpm. The formed flocs were allowed to settle for 120 min. In the process of sedimentation the volume with sludge occupying the 100 ml cylinder, was recorded every 30 minutes. The data received contributed in defining the sludge volume index (SVI). The sludge volume index is the volume in milliliters occupied by 1 g of a suspension after 30 min of settling. To determine the size of the coagulate particles the Laser Particle Sizer ANALYSETTE 22 NanoTec (Fritsch GmbH, Germany) with measuring range of 10 nm - 1 mm and Leica MZ 16 A stereomicroscope (Leica Microsystems (Switzerland) Ltd.) were used. The results are represented as a percent of complete sample volume, that is filled with particles with defined diameter and as a percent of mass content of defined particles fraction.

After 120 minutes of sedimentation, the system was filtered through a glass filter with a pore size of less than 16 μm. The filtered sludge was drained of for 24 hours at 103°C. The dried coagulates (HLES-Al) were quantatively and qualitatively characterized by scanning electron microscope (SEM) with energy dispersive X-ray analysis (EDX) (Mira/LMU Schottky, Inca Energy 350 Oxford Instruments), Fourier Transform Infrared (FT-IR) and Carbon Nuclear Magnetic Resonance ($^{13}$C-NMR) spectroscopy. For HLES-Al characterization FT-IR spectra was obtained on a FT-IR spectrophotometer (Perkin-Elmer Spectrum One) with KBr discs containing samples. $^{13}$C-NMR spectra of HLES-Al was recorded on a Bruker 300MHz spectrometer from 150 mg of sample dissolved in 4% NaOD (1.0 mL). The NMR spectrum was acquired by applying a 90° pulse width, a 0.238 s acquisition time, a 2.0 s pulse delay, and $^{1}J_{C\text{–}H}$ of 145 Hz. In particular, 24 576 scans were used for the acquisition of $^{13}$C-NMR spectra of coagulate.

## III Results and discussion

In the coagulation process, the settling speed of the flocs formed is important since it would influence the overall cost and efficiency.

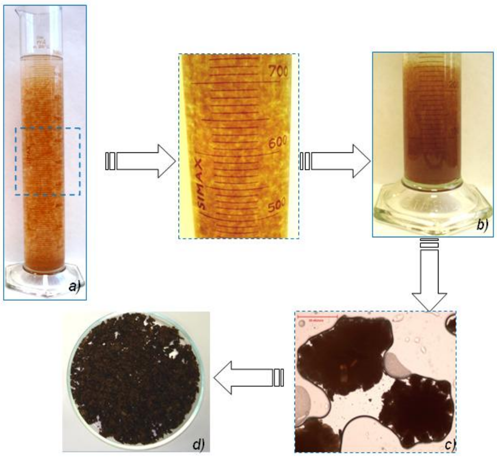


Fig. 1. HLES-Al coagulates formation process: a – beginning of sedimentation, b– coagulates developed, c – coagulates particles (Leica MZ 16 A stereomicroscope), d - dry coagulate

In order to evaluate this parameter, the settling time was recorded for the flocs formed in order to reach half of the solution's level. COMPAC exhibited excellent settling characteristics with majority of the flocs settled out in the initial 20-30 min of settling. The sludge volume index is 89 ml g$^{-1}$. A value less than 140 ml g$^{-1}$ is considered a good settling sludge. Coagulate HLES-Al is characterized by high moisture - 98.2%.

The research of coagulates granulometric composition (Fig. 2) followed by the fact that the coagulate particles' sizes are ranging from 2 to 246 μm. Analyzing the data obtained, it can be concluded that 53% of the particles' size is between 40 and 100 μm, 22% of the particles - 16-40 μm and 25% of the particles have a size of 100 μm. By contrast, smaller particles (<16 μm) is 1%. The average particle size is equal to 45.8 mm.

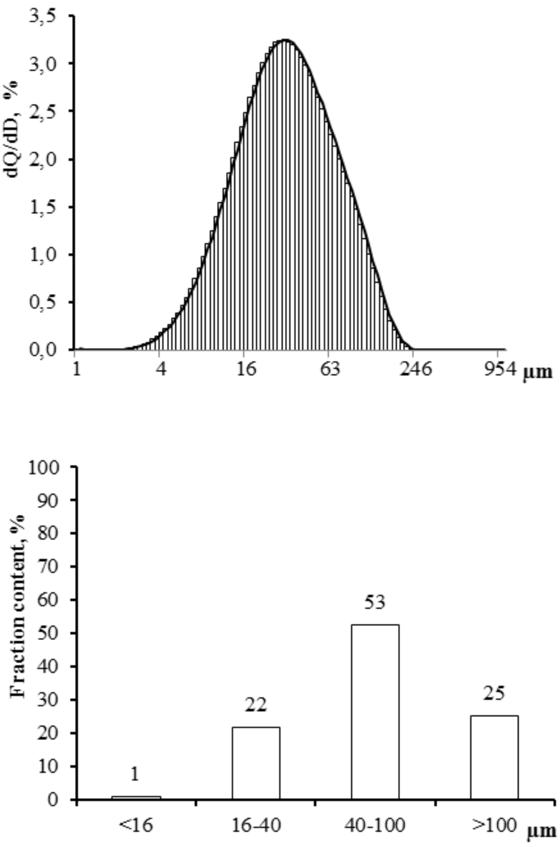


Fig. 2. Coagulate's granulometric composition

Coagulates elemental composition is shown in Table 2. The derived coagulate is composed primarily of carbon (27.9%), oxygen (49.4%). The aluminum, the metallic element that arised from the agent used for coagulation and sedimentation of the sludge, dominated among the inorganic elements of sludge.

TABLE I

Coagulate elemental composition

| C, % | O, % | H, % | N, % | Al, % | Na, % | Cl, % |
|---|---|---|---|---|---|---|
| 27.9 | 49.4 | 4.3 | 0.3 | 10.9 | 4.1 | 3.1 |

Carbon, oxygen and hydrogen are referred to organic components of coagulate, namely, to the pollutants of wood origin the deposition of which is of aluminum-containing coagulant. The deposited pollutants of wood origin are characterized by a high content of hemicellulose (75-80%).

The structural characteristics of coagulates were studied by means of FT-IR and $^{13}$C-NMR methods.

The FT-IR of coagulate are illustrated in Fig. 3.

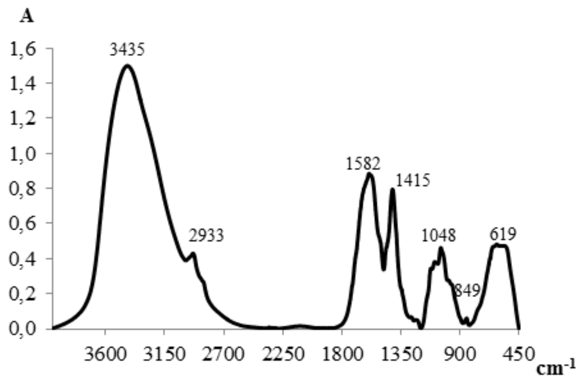


Fig. 3. FT-IR spectra of HLES-Al coagulate

A strong broad band at 3435 cm$^{-1}$ was due to the stretching of hydroxyl groups, and the behaviour of these spectra in the 2934 cm$^{-1}$ region shows the C–H stretch in methyl and methylene groups. Intensive peak at 1567 cm$^{-1}$ characterise COO- skeletal vibrations in glucuronic acid. The wave number characteristic for typical xylan is 1046 cm$^{-1}$ [14]. The adsorption at 1414 cm$^{-1}$ are originated from aromatic skeletal vibrations in associated lignin [15].The absorbance at 849 cm$^{-1}$ was attributed to β - glycosidic linkages between the sugars units. According to the coagulum FT-IR spectra the aluminum interaction with HLES occurs with HLES - Al coordination sites formation. Coordination takes place through HLES-OH and -COOH groups evidenced by the absorption band 619 cm$^{-1}$ in the region characteristic of Al-O-link [16].

The $^{13}$C-NMR spectra of coagulate are illustrated in Fig. 4.

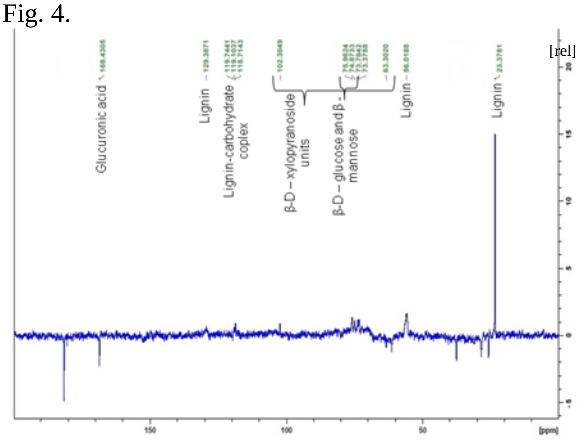


Fig. 4. $^{13}$C-NMR spectra of HLES-Al coagulate

The signal at 23.3 ppm is most likely due to -$CH_3$ from acetyl groups in hemicelluloses and lignin [17]. The shift at 56.02 ppm is attributed to the presence of methoxyl groups of the aromatic rings of guaiacyl and syringyl units in lignin and methoxyl group of a 4-O-methyl-D-glucuronic acid residue in the xylan [18]. The peaks at 102.3, 75.9, 73.7, 73.3 and 63.3 ppm, which are attributed to C-1, C-4, C-3, C-2 and C-5 of β-D-xylopyranoside, respectively, confirmed the (1-4)-β-D-xylopyranoside linkage. The signals at 74.9 corresponds to C-3 of α-L-arabinofuranosyl residues linked to β-D-xylans [17]. However the signals at 74.9-75.9 ppm may be assigned to C-3 in β-glucose and C-5 in β-mannose [19]. The peaks 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-hydroxyphenyl units [15]. The chemical shifts at 168.4 ppm represents the C-6 of glucuronic acid residues [19]. The presence of quantities of associated lignin was identified by one weak signal at 182.0 ppm, which originates from the carbonyl group in associated lignin [20].

This finding demonstrated that involved in the Al-coagulate are composed, mainly, of O-acetil-4-O-metil-D-glucuron-β-D-xylan with the presence of small amounts of β-(1-4) linked glucomannose.

The derived HLES Al-coagulate may be considered as material, causing scientific and practical interest. Taking into account that the given coagulate is a waste of many tons, the question of its disposal or recycling is very topical.

## IV CONCLUSION

Using the aluminium-containing composition coagulant based on polyaluminium chloride, coagulate is characterized by a low sludge volume index (89 ml g$^{-1}$). The optimal time of sedimentation is 20-30 minutes. The coagulate particles have an average size of 45.8 μm. The deposited pollutants of wood origin are characterized by a high content of hemicellulose (75-80%). It is concluded that the hemicelluloses in the HLES-Al coagulate are characterized by O-acetyl-4-O-methyl-D-glucuron-β-D-xylan and with β-(1-4)-glucomannose. The derived coagulate is composed primarily of carbon (27.9%), oxygen (49.4%) and aluminum (10.9%). Taking into account non-toxicity of hemicelluloses and the low aluminum content, the coagulate obtained is not seen as an intended one for disposal waste, but as a by-product, that can be used successfully in various industries.

## V ACKNOWLEDGEMENT

The researches leading to these results have received funding from the Latvian Council of Science for a grant n$^{o}$ 09-1610c, as well as from the European Social Fund within the project „Support for the implementation of doctoral studies at Riga Technical University.

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