

J. Brovkina<sup>1</sup>, G. Shulga<sup>1</sup>, J. Ozolins<sup>2</sup>, B. Neiberte<sup>1</sup>,  
A. Verovkins<sup>1</sup>, V. Lakevics<sup>2</sup>

<sup>1</sup> Latvian State Institute of Wood Chemistry, Dzerbenes Street 27, LV-1006Riga, Latvia

<sup>2</sup> Riga Technical University, Faculty of Material Science and Applied Chemistry, Paula Valdena Street 3/7, LV-1048Riga, Latvia

## INTRODUCTION

The wood hydrothermal treatment is one of the plywood production's stages, which resulting in the production of wastewater containing such components as hemicelluloses, lignin and wood extractive substances (HLES). It is necessary to improve the wastewater treatment technology with the aim to enhance the yield of sludge from plywood wastewater for its effective and rational recycling. In the present study, the optimal coagulation conditions for the HLES removal have been found using the developed aluminium salt-based coagulant. However, the proposed treatment technology generates many tons of wood-originated sludge – a biomass coagulate. Therefore, the study aim was to show the effectiveness of usage of the developed inorganic composite coagulant based on PAC for plywood wastewater treatment procedure and to present a perspective trend in the possible application of the obtained wood-originated sludge.

## MATERIALS AND METHODS

The wastewater sample has been presented by a model solution obtained via the hydrothermal treatment of the birch wood sawdust. For the treatment of the model solution, the new developed composite coagulant (KHPAC) based on PAC and aluminium chloride ( $\text{AlCl}_3$ ) was used. Coagulation efficiency was evaluated by a residual concentration of HLES after 2 hours. Characterisation of the wood-originated coagulate was based on sizes of the air-dried coagulate granules, functional, structural and elemental composition.

The obtained wood-originated sludge in the form of a coagulate was used as an active additive to improve a Latvian Triassic clay (LTM) from the Vadakste deposit for obtaining a sorbent. The modification of clay granules with sizes between 0.25 mm and 3 mm was performed by spraying a coagulate solution with a concentration of 1.8–1.9 % to the clay surface. The treated clay samples were dried at 105 °C for 24 hours. Then, the modified samples were thermally treated at 800 °C in a high temperature furnace for 2 hours. The sorption efficacy of modified clay was investigated by performing tests on water (oil) carrying capacity and sorption of the heavy metals from the solutions.

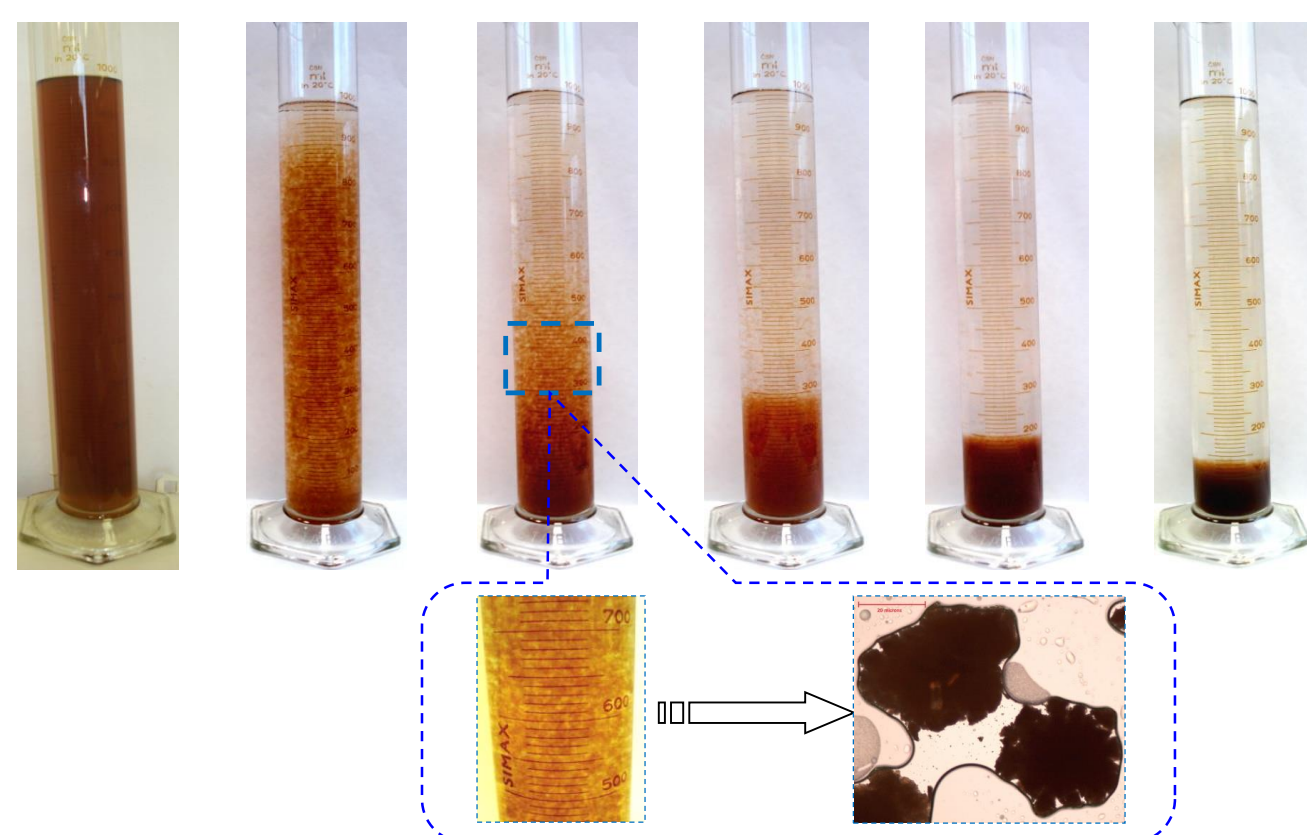
## RESULTS AND DISCUSSIONS

### HLES removal by coagulation

Parameters	Value
Hemicelluloses, lignin and wood extractive substances (HLES)	1400 mg L <sup>-1</sup>
Lignin containing substances (LCS)	280 mg L <sup>-1</sup>
Chemical Oxygen Demand (COD)	1285 mgO L <sup>-1</sup>
Total Organic Compounds (TOC)	732 mg L <sup>-1</sup>
Colour	746 mg L <sup>-1</sup> Pt <sup>-1</sup>

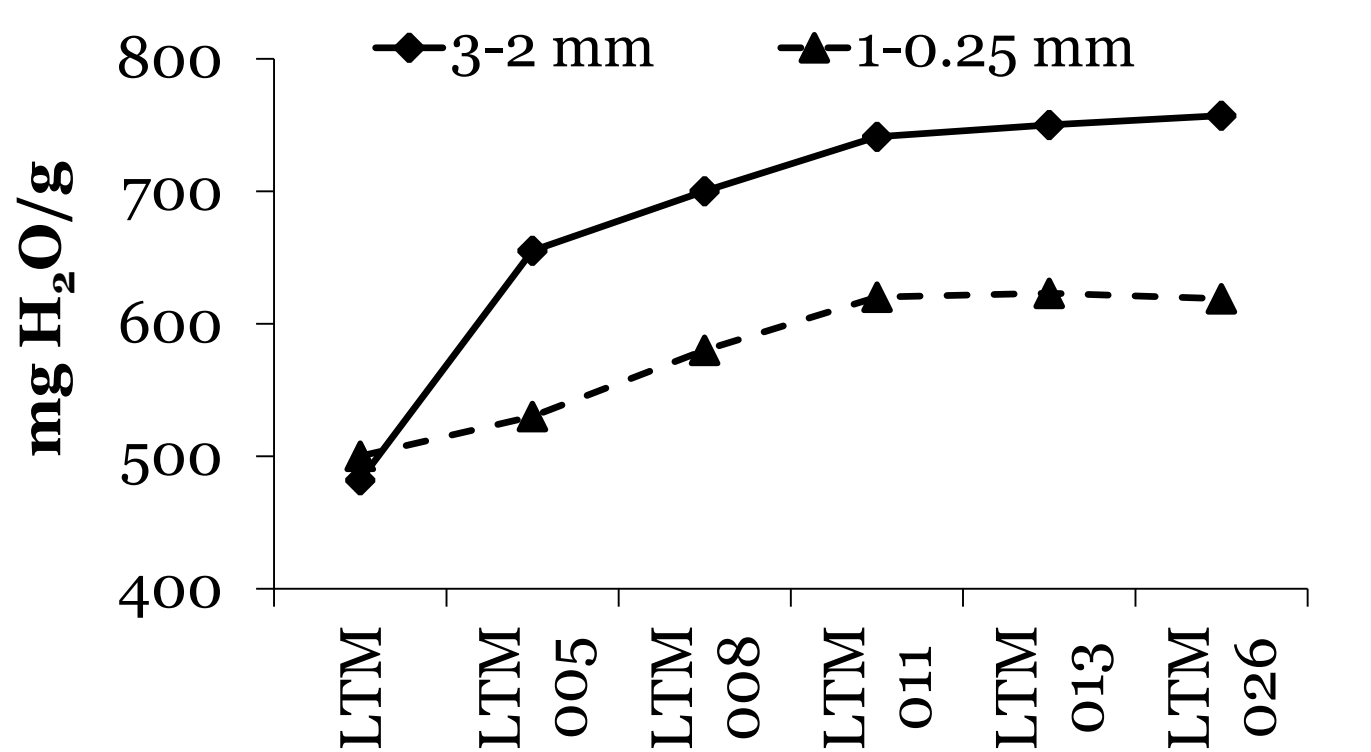
According to the obtained results, an optimal composition of the new coagulant, characterised by the maximal efficiency of the HLES removal (92%) in the wide temperature (13–40°C) interval, is a composition, in which 50% of the PAC content is replaced by  $\text{AlCl}_3$ . The new coagulant is not particularly sensitive to temperature. It is found that the removal efficiency of the HLES and LCS with the new coagulant depends on pH value, and the optimal pH range varies from 6.0 to 7.0. The optimal dosage varies from 75–125 mg L<sup>-1</sup>. The removal efficiency of the HLES, LCS, COD and colour is 91%, 65%, 47% and 90%, respectively. Besides, the treated wastewater after filtration is characterised by a lower concentration of the residual aluminium ions.

### Wood-originated coagulate

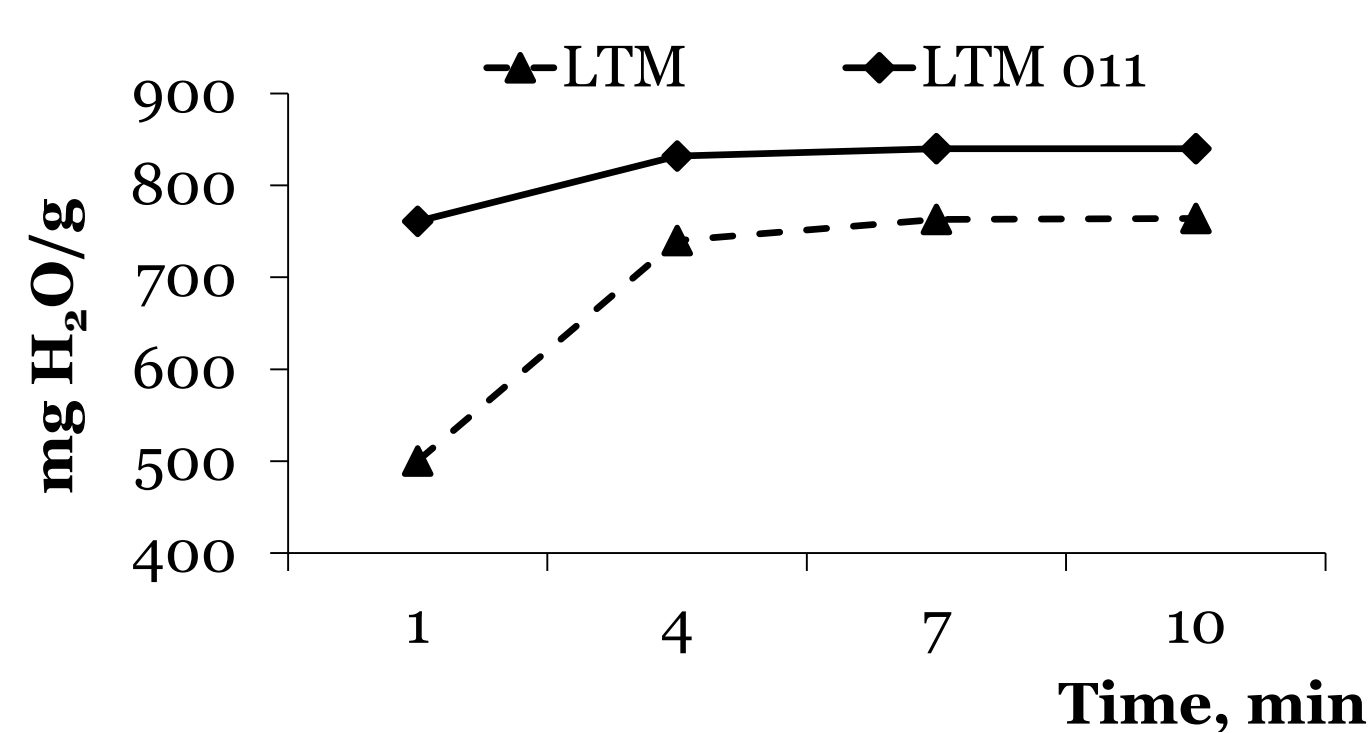


The air-dried coagulate sample was characterized by a size of particles between 2 to 246 μm, but an average size was equal to 45.8 μm. The obtained coagulate is composed primarily of carbon (27.9%) and oxygen (49.4%). The aluminum and sodium dominated among the inorganic elements in its elemental composition. The chemical analysis has shown that it contained 75% hemicelluloses, 14% lignin-containing substances and 11% extractives. The analysis of <sup>13</sup>C-NMR spectrum of the coagulate has shown that the main component of hemicelluloses is O-acetyl-4-O-methyl-D-glucuron-β-D-xylan with the presence of small amounts of β-(1-4) linked glucomannose.

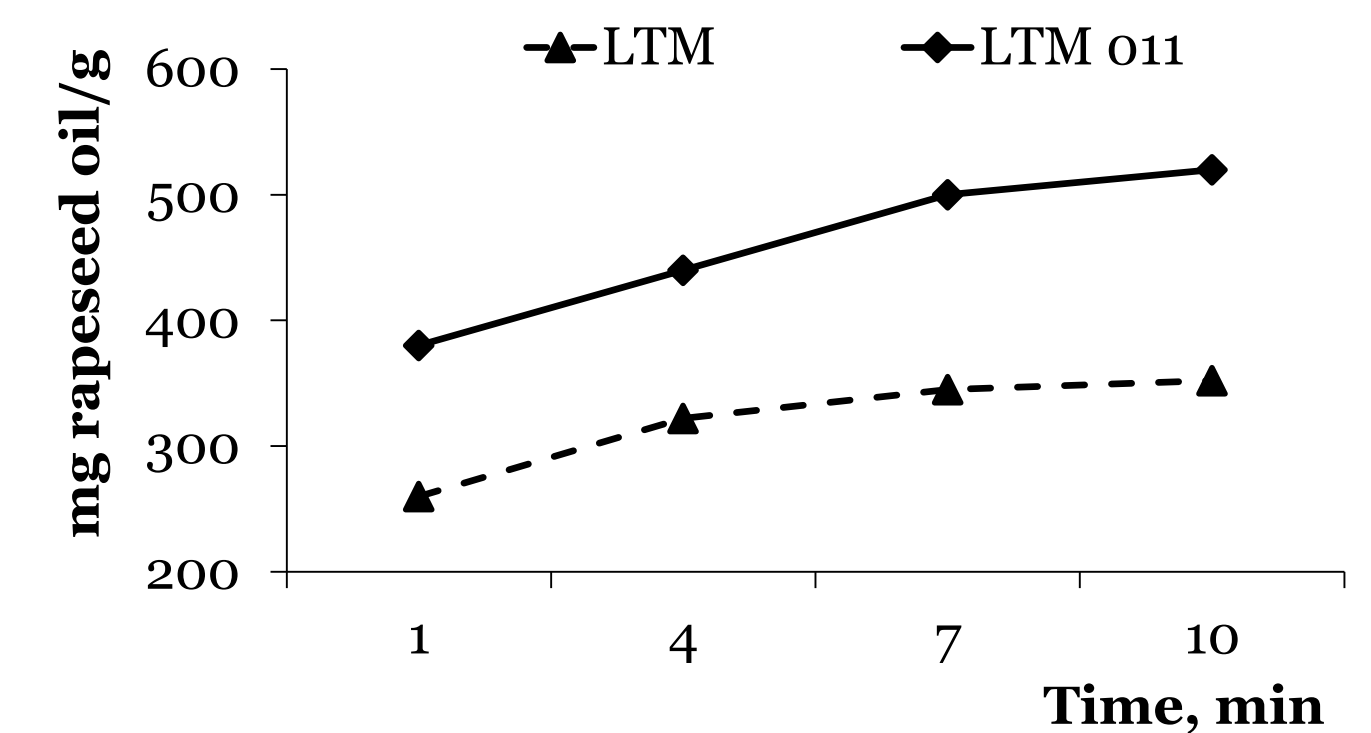
### Determination of sorption capacity by modified clay samples



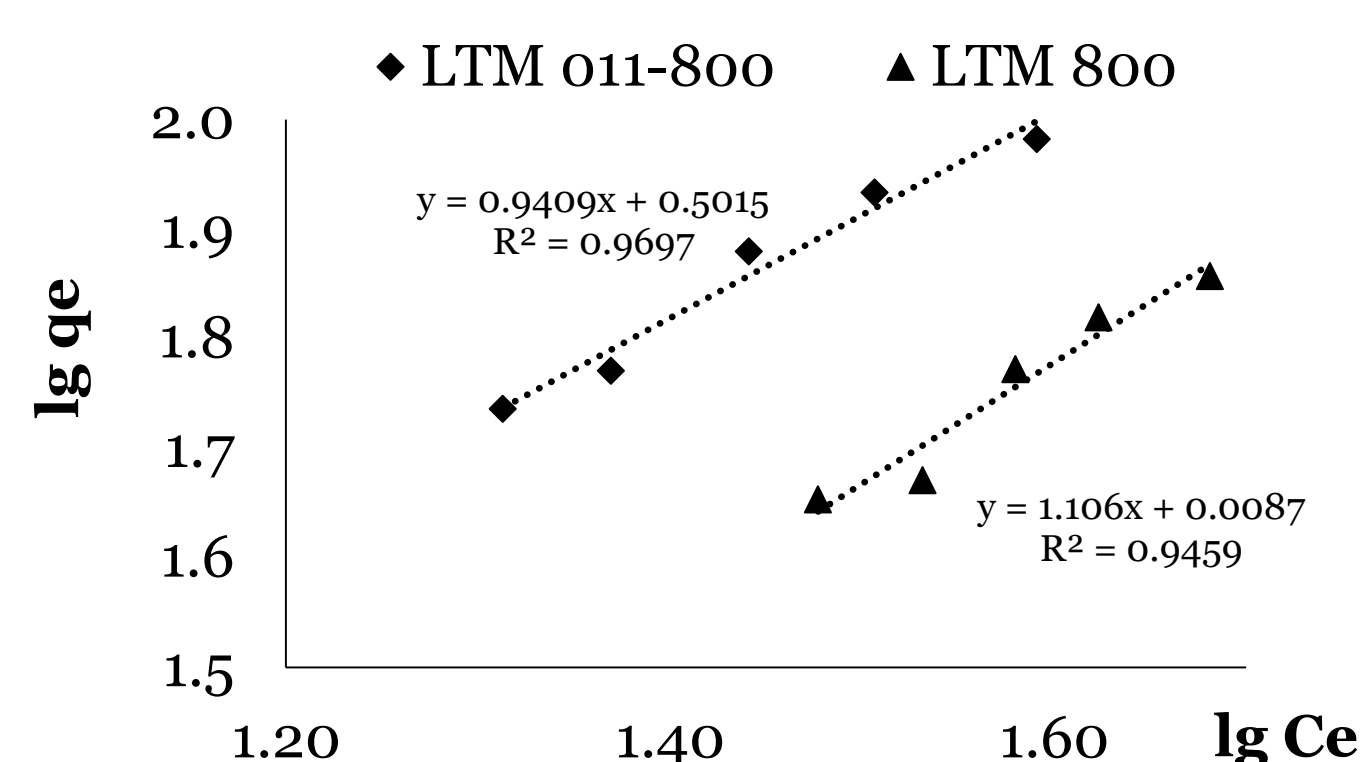
The obtained results show that a better water carrying capacity of 740 mg H<sub>2</sub>O per 1 g of clay is found for the modified sample (LTM 011) granules with the sizes between 2.0 and 3.0 mm. This value is 35% higher than the capacity for the control LTM clay sample.



It is seen that the water sorption is higher for the modified clay sample than for the control clay that could be explained by the presence of hydrophilic hemicelluloses fragments presented in the modified sample.



Based on the data obtained, the oil binding capacity of the LTM control and LTM 011 sample is lower than their water sorption results. Evidently, both the hydrophilicity of clay and the enhanced oil viscosity could be a reason of the lower sorption values. At the same time, the rapeseed and silicone oil binding capacity of the modified sample is higher by 32% and 21%, respectively, compared to the LTM sample.



After a 24-hour study, the concentration of zinc ions from water solution was reduced. The sorption efficiency was 60% and 72% for the unmodified and modified clay samples, respectively. The present study results indicated that the Freundlich model fit the experimental data well. Therefore, it can be concluded that, for the adsorption of Zn<sup>2+</sup>, the modified clay sample is more powerful. The same tendency was observed for Cu<sup>2+</sup>.

The wood originated coagulate, obtained as a result of the treatment of the model solution with the new composite coagulant, was characterised by sizes of the particles and a chemical composition. The formed wood-originated coagulant was used as an additive for obtaining clay sorbents. Water carrying capacity of the modified clay increases by 35% in comparison with the unmodified sample. The sorption capacity of the modified clay for a rapeseed and silicone oil increases by 31% and 21%, respectively, relative to the unmodified clay. The heavy metals sorption capacity for the modified clay also increases by 10–12 %. These results testified that the wood-originated sludge formed as a result of plywood wastewater treatment can be applied in the obtaining of environmentally friendly and inexpensive clay-based sorbents.