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The advanced application of the wood-originated wastewater sludge

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Abstract. 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. The developed composite coagulant is characterized by lower doses, a wide range of the work pH values, the insensitivity against temperature changes and a higher coagulation efficacy compared with traditional aluminium salts. The proposed treatment technology generates many tons of wood-originated sludge – a biomass coagulate. It was found that the formed coagulate produced in the process of wastewater treatment can increase the sorption ability of clay. The optimal content of the dry coagulate in a clay sorbent does not exceed 0.11%. The sorption capacity of the developed sorbent for water, rapeseed and silicone oil increases by 35%, 31% and 21%, respectively, relative to the unmodified clay sorbent. The sorption efficiency of heavy metals from water solutions is also increased by 10–12%. The thermal treatment of the modified clay sorbent at the high temperature leads to an increase in its sorption capacity for oil products.

Key words: coagulation, composite coagulant, woodworking wastewater, sludge, clay sorbent.

INTRODUCTION

The plywood industry is an industrial sector where a high amount of wood materials and water is used during the manufacturing process. One of the stages of raw material preparation is the hydrothermal treatment of wood. Wastewater of hydrothermal basins are characterized by the high degree of contamination. The presence of lignin and its derivatives, as well hemicelluloses and extractive substances (HLES) contribute to strong colour of wastewater, turbidity and high chemical oxygen demand (COD).

There are different treatment methods for removing organic and inorganic substances from wastewater. They include biological treatment (Viraraghan, 2004; Leiviska et al., 2008; Buyukkamaci & Koken, 2010), various membrane technologies (Chen et al., 2015; Doruk et al., 2016), electrochemical methods (Chanworrawoot &

Hunsom, 2012), chemical oxidation (Kishimoto et al., 2010), physicochemical methods (Ganjidoust et al., 1997; Ashrafi et al., 2015) or combination of them (Klauson et al., 2015; Hubbe et al., 2016; Brink et al., 2018).

One of the most used methods for wastewater treatment is a coagulation/flocculation process. The coagulation/flocculation method is not only an economic, but also an effective mode for removal of COD and colour from the wastewater. The chemical coagulants such as inorganic metal salts (aluminum and ferric salts) and polyelectrolytes (Sharma et al., 2006; Lee et al., 2014) are often used in the coagulation/flocculation process.

It is known that polyaluminium chloride (PAC) is a more effective coagulant than aluminium sulphate and aluminium chloride for paper and pulp mill wastewater treatment (Kumar et al., 2011; Aziz et al., 2017). PAC faster forms flocs due the high positive electrical charge that allows it easily reducing the electrical charge on the surface of colloidal particles. At the same time, PAC is a more expensive coagulant in comparison with the classic aluminium salts used for wastewater treatment.

To enhance the efficiency of the coagulation, PAC is used in compositions with different chemical reagents, for example, calcium oxide and chloride (Palone et al., 2011), iron oxides or halogenides (Lee et al., 2008), with a cationic flocculant, for example, polyacrylamide (Lukerchenko, 2008; Katrivesis et al., 2019). There are also known two-stage coagulation method, firstly with aluminium sulphate and then with polyaluminium chloride (Kevin et al., 2004). However, such the method is complicated from the technological point of view due to the multistageness of the coagulation process.

The main drawbacks of the coagulation method are its sensitivity to pH and low temperature (Toczyłowska-Mamińska, 2017), as well as high volumes of the formed sludge that is defined by a wastewater composition, a type and a dosage of the applied coagulant and process conditions.

Due to the increased requirements for water environmental, it is very important to regenerate industrial wastewater sludge for obtaining new products with added value. The effective usage of sludge is an actual challenge for each industry, where a wastewater treatment technology is applied. It is known that wastewater sludge can be used as a biofuel (Seiple, 2017), for soil recovery (Lakhdar et al., 2010) and agricultural needs (Mtshali, 2014), for bricks production (Lin & Weng, 2001), in road layers (Lucena et al., 2014), for cements and concretes manufacturing (Barrera-Díaza et al., 2011), as fertiliser (Lazdina et al., 2011) and as a sorbent (Rio et al., 2006; Smith et al., 2009).

Methods of combining wastewater sludge with other natural materials are already widely used. Manufacturing of such sorbents is traditionally based on the chemical activation of components and the further thermal treatment. There are methods for a recycling of wastewater sludge with wood chips, cement, lime, slag, mineralized refuse and construction waste (Kamon et al., 2002; Kim et al., 2005; Ma et al., 2007; Fang et al., 2010; Zhou et al., 2011). The obtained sorbents of these types are efficient and cheap. The clay based materials often correspond to the above mentioned requirements and are characterized by low cost and high specific surface (Lakevics et al., 2011).

The increasing interest towards modified clays is related to the necessity to create environmentally safe sorbents. Clay modification can be done by using of inorganic acids and metal salts (Ismadji et al., 2015), humic acid (Jemeljanova et al., 2019), aluminium and iron polyhydroxy complexes (Khankhasaeva et al., 2006), chitosan

(Unuabonah et al., 2017) and organic additives (Olalekan et al., 2010). Clay based sorbents can be used for discoloration of rapeseed oil (Frost Ray et al., 2007), sorption of dyes (Ho et al., 2001) and heavy metals (Carvalho et al., 2007).

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

Model wastewater

The wastewater sample has been presented by a model solution obtained via the hydrothermal treatment of the birch wood sawdust (Brovkina et al., 2010). The main parameters of the model solution are listed in the Table 1.

Table 1. Model wastewater physico-chemical characteristics

Parameters	Value
Hemicelluloses, lignin and wood extractive substances (HLES)	1,400 mg L^{-1}
Lignin containing substances (LCS)	280 mg L^{-1}
Chemical Oxygen Demand (COD)	1,285 mg O L^{-1}
Total Organic Compounds (TOC)	732 mg L^{-1}
Colour	746 mg L^{-1} Pt^{-1}

Coagulation process

For the treatment of the model solution, the new developed composite coagulant (KHPAC) based on PAC and aluminium chloride ($AlCl_3$) was used (Shulga et al., 2014). The efficacy of the coagulation was compared with the parameters of the model solution obtained after treatment with PAC, aluminium chloride and composite coagulant, containing PAC and aluminium sulphate (KSPAC) (Shishkin, 2004).

The jar test procedures was carried out using 50 mL of the model wastewater and 50 mL of a coagulant solution. Sample was stirred at 200 rpm for 1 minute and then for 2 minutes at 40 rpm. The flocs formed during coagulation were allowed to settle for 120 minutes. Coagulation efficiency was evaluated by a residual concentration of HLES, which comprised hemicelluloses, lignin-containing substances (LCS) and extractives. For their determination, the analytical chemistry methods developed at the Latvian State Institute of Wood Chemistry (Zakis & Neiberte, 2003) were used. Each experiment was carried out three times. The results are presented as mean values.

Characterisation of the wood-originated coagulate

Sizes of the air-dried coagulate granules were measured with the Laser Particle Sizer ANALYSETTE 22 NanoTec (Fritsch GmbH). The functional and structural composition of the coagulate was studied with Carbon Nuclear Magnetic Resonance (^{13}C-NMR) (Bruker 300MHz spectrometer) and Fourier Transform Infrared spectroscopy (FT-IR) (Perkin-Elmer Spectrum One). The elemental composition of the wood-originated coagulate was studied using catalytic combustion process (Elementar Analysensysteme GmbH, Germany).

Clay modification with coagulate

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. The dry coagulate content in the clay samples varied from 0.05 to 0.26%. The modified clay samples were labeled as: LTM 005 (0.05% coagulate content), LTM 011 (0.11% coagulate content), etc. Then, the modified samples were thermally treated at 800 °C in a high temperature finance for 2 hours. After this procedure, the clay samples were labeled as: LTM–800 (unmodified thermally treated sample at 800 °C); LTM 011–800 (modified thermally treated sample at 800 °C with a 0.11% coagulate content).

Determination of water carrying capacity by modified clay samples

To determine the water carrying capacity a glass tube with porous bottom was used. The tube filled with clay sample was kept in water for 15 minutes. The water level was 1 cm above the clay level in tube. After contact time the tube was removed and weighed. The water carrying capacity (W, mg H_2O g^{-1}) was calculated using follow equation (1):

$$W = \frac{m_3 - m_2}{m_2 - m_2} \cdot 1{,}000 \quad (1)$$

where m_1 – tube mass, g; m_2 – tube and clay mass, g; m_3 – tube and treated clay mass, g.

Each experiment was carried out two times. The results are presented as mean values.

Determination of water (oil) binding capacity by modified clay samples

A clay sample of 5 ± 0.05 g was deposited on a metal sieve using filter paper. The sieve was submerged in water (or oil), so that the sample was held from 1 to 15 minutes. For studying oil binding, rapeseed and silicone oils were used. After this time, the sieve with the clay sample was removed from the water (or oil) and left to drain for 2 minutes. The water (oil) binding capacity (A, mg H_2O (or oil) g^{-1}) was calculated using follow Eq. (2):

$$W = \frac{m_3 - m_2 - m_1}{m_2} \cdot 1{,}000 \quad (2)$$

where m_1 – control experiment with submersion without clay, g; m_2 – dry clay sample mass, g; m_3 – mass of the sieve, filter and clay after the saturation with water (oil), g.

Each experiment was carried out two times. The results are presented as mean values.

Determination of heavy metal ion sorption

The adsorption experiments were carried out by adding the clay samples to water solutions, containing copper chloride and zinc chloride, for 24 hours. Residual zinc and copper concentrations in water solutions were determined by flame atom absorption spectrometry at the wavelengths of 324.8 nm and 213.9 nm, respectively, using the calibrated curves for copper and zinc chloride water solutions. A single measurement was performed.

The amount of metal adsorbed at equilibrium, q_e (mg g^{-1}) was calculated by the following mass balance relationship:

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (3)$$

where C_0 and C_e – initial and equilibrium metal concentrations, mg L^{-1}; V – volume of the solution, L^{-1}; m – mass of the adsorbent, g.

To predict the adsorption, process the Freundlich isotherm model was applied to experimental data. The Freundlich isotherm model describes the reversible adsorption, which can be applied to multilayer adsorption, on the basis of surface heterogeneity. The linear form of the Freundlich isotherm equation can be expressed as follows:

$$\log q_e = \log K_F + \frac{1}{n} log C_e \quad (4)$$

where q_e a – amount of metal adsorbed at equilibrium, mg g^{-1}; C_e – equilibrium metal concentrations, mg L^{-1}; n – constant which measure adsorption intensity; K_F – constant which is related to adsorption capacity.

RESULTS AND DISCUSSION

HLES removal by coagulation

Early, it was found that optimal pH value for the HLES removal by the aluminium salts was 5.0–6.0 (Brovkina et al., 2011). At pH 6.0, the critical coagulation concentration was 170 mg L^{-1} for $Al_2(SO_4)_3$, 65 mg L^{-1} for $AlCl_3$ and 100 mg L^{-1} for PAC at temperature 20°C. The residual concentration of aluminium system after treatment varied from 0.07 mg L^{-1} to 0.45 mg L^{-1}, depending on a type of aluminium salt. The settling time was 50–60 minutes for $Al_2(SO_4)_3$, 30–40 minutes for $AlCl_3$ and 10–20 minutes for PAC. At a relatively lower temperature (13°C), the HLES removal was 60%, 62% and 80% in the present of $Al_2(SO_4)_3$, $AlCl_3$ and PAC, respectively. The residual concentration of aluminium ions after the treatment with these salts was 0.62 mg L^{-1}, 0.26 mg L^{-1} and 0.09 mg L^{-1}. A higher recovery of the HLES, a lower residual concentration of aluminium ions in water, a smaller settling time and a non-sensitivity to the temperature changes indicated that PAC was a more effective coagulant for the HLES than $Al_2(SO_4)_3$ and $AlCl_3$.

Table 2. HLES removal depend on KHPAC composition and temperature

Mass balance between PAC and $AlCl_3$	Temperature, °C		
	13 °C	20 °C	40 °C
50%PAC+50%$AlCl_3$ ($KHPAC_{50}$)	92	95	88
40%PAC+60%$AlCl_3$ ($KHPAC_{40}$)	86	95	88
20%PAC+80%$AlCl_3$ ($KHPAC_{20}$)	77	75	74
10%PAC+90%$AlCl_3$ ($KHPAC_{10}$)	77	85	85
100% $Al_2(SO_4)_3$	60	81	81
100% $AlCl_3$	62	81	80
100% PAC	80	80	82

In Table 2, the results of the usage of the new composite coagulant with a different mass ratio between PAC and $AlCl_3$ for removing the HLES and LCS from the model wastewater, depending on a temperature of the treatment, are shown.

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 interval, is a composition $KHPAC_{50}$,

in which 50% of the PAC content is replaced by $AlCl_3$. It is known that a low temperature has a negative effect on the efficacy of a coagulation process. The coagulation at lower temperatures requires a higher dosage and a bigger contact time forflocs sedimentation. However, from the data obtained, $KHPAC_{50}$ 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 (Fig. 1).

In comparison with PAC, the new coagulant increases HLES and LCS removal on 12% and 14%, respectively, at pH 6.0. In the case of pH 7.0, the removal efficacy of these pollutants increases by 50% and 25%. Taking into account that the residual aluminium concentration has higher values in the wastewater at pH ≥ 7, the optimal pH value for the usage of the new coagulant is 6.0.

The results of the model wastewater treatment with the new coagulant ($KHPAC_{50}$) and the known KSPAC composite coagulant, composed from PAC and aluminium sulphate, at pH 6.0 and a temperature of 14°C are shown in Fig. 2.

According to the obtained results, the new coagulant demonstrates a higher degree of removal of the HLES and LCS from the model wastewater than the composite coagulant KSPAC. Besides, the treated wastewater after filtration is characterised by a lower concentration of the residual aluminium ions (Fig. 3).

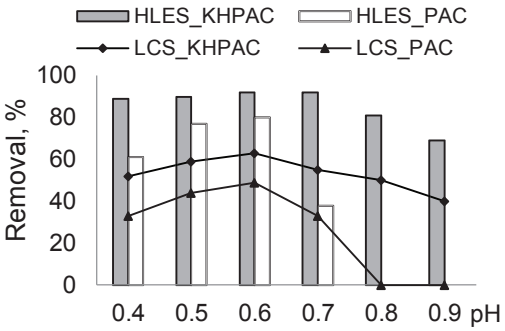

Figure 1. HLES and LCS removal with PAC and the new cogulant depending on pH.

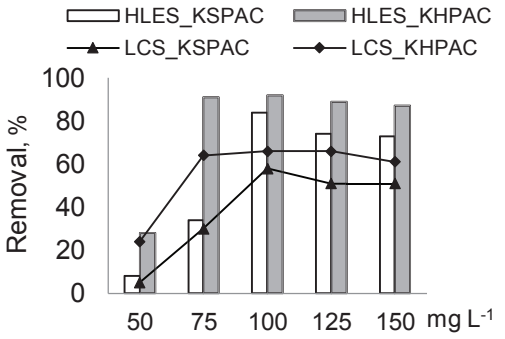

Figure 2. HLES and LSV removal in the model in the wastewater treated with the new and the known coagulant at temperature 14 °C and pH 6.0.

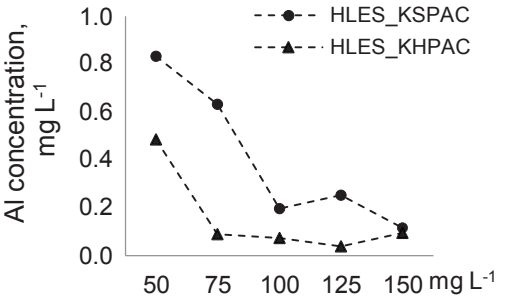

Figure 3. Residual aluminium concentration treated model wastewater at 14 °C and pH 6.0.

The optimal KHPAC dosage varies from 75–125 mg L^{-1}. The removal efficiency of the HLES, LCS, COD and colour is 91%, 65%, 47% and 90%, respectively.

The visual dynamic of the wood biomass settling during the coagulation/flocculation process can be seen in Fig. 4.

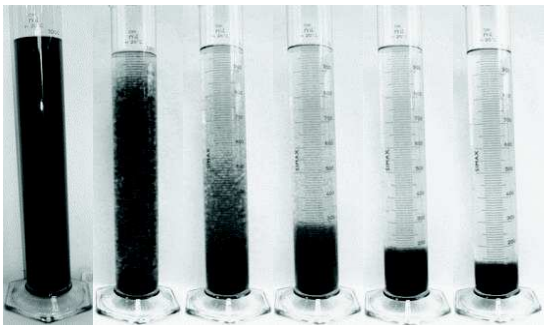

Figure 4. Formation of the wood-originated coagulate in the model wastewater treated with the new composite coagulant during 30 minutes.

Characterisation of the wood-originated coagulate

According to the results obtained with the Laser Particle Sizer device, 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 (Fig. 5).

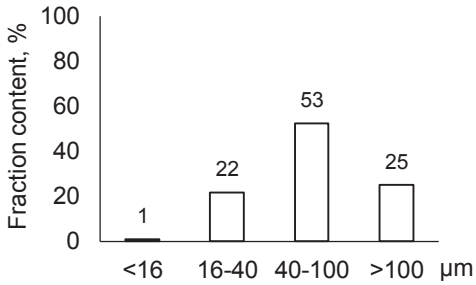

Figure 5. Wood-originated coagulate's granulometric composition.

The precipitated coagulate was characterised by the elemental composition presented in Table 3. The obtained coagulate is composed primarily of carbon (27.9%) and oxygen (49.4%). The aluminum and sodium arising due to the presence of the composite coagulant in the flocs dominate among the inorganic elements in the elemental composition.

The chemical analysis of the coagulate, performed according to the developed procedures (Zakis & Neiberte, 2003). The coagulate contained 75% hemicelluloses, 14% lignin-containing substances and 11% extractives.

Table 3. Wood-originated coagulate's elemental composition

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

The previal content of hemicelluloses in the obtained coagulate are testified by FT–IR and ^{13}C–NMR spectroscopy.

Following the FT–IR spectrum (Fig. 6, a), the presence of the intensive peak at 1,567 cm^{-1} characterises COO– skeletal vibrations in glucuronic acid. The characteristic wave number for typical xylan is 1,046 cm^{-1}. The absorbance at 849 cm^{-1} was attributed to β-glycosidic linkages between the sugars units. It can be assumed that the interaction between aluminum and HLES takes place via HLES–OH and HLES–COOH coordinate

bonds formation. This testifies the presence of the absorption band at 619 cm^{-1} in the region, in which Al coordinate bonding appears.

The analysis of ^{13}C–NMR spectrum (Fig. 6, b) of the coagulate shown that the main component of the sample was hemicelluloses (75–80%) in the form of O–acetyl–4–O–methyl–D–glucuron–β–D–xylan with the presence of small amounts of β– (1–4) linked glucomannose.

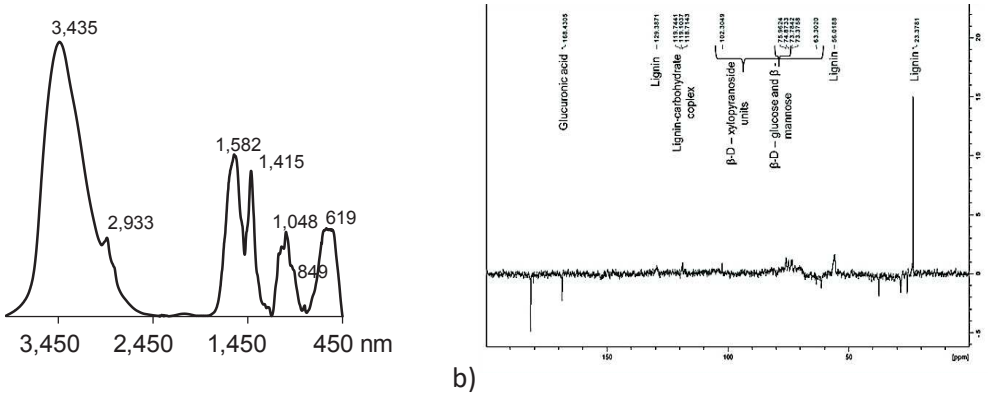

Figure 6. FT–IR (a) and ^{13}C–NMR (b) spectra of the wood-originated coagulate's.

Determination of water carrying capacity by modified clay samples

The clay modification leads to changing its fractional composition depending on the amount of the added coagulate. After adding 0.11% of the dry coagulate, the fraction content with grain diameter > 3 mm increased 6 times, but the fraction with grain size 1.00 < d < 0.25 mm decreased by 5 times in comparison with control (the clay treated with pure water).

The further study was related to determination of water carrying capacity according to the methods described in the experimental part. The obtained results show (Fig. 7) that a better water carrying capacity of 740 mg H_2O 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. The further increasing of the coagulate amount in the clay doesn't impact on water carrying capacity. This effect can be explained by the presence of the hydrophilic groups in the biomass coagulate.

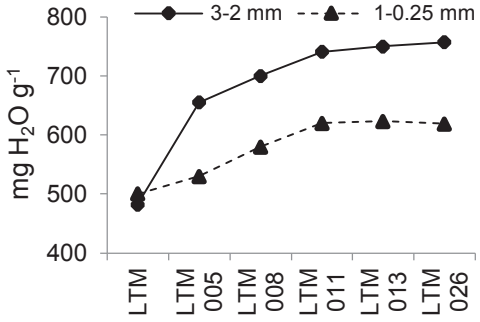

Figure 7. water carrying capacity of the control and modified clay samples depending on coagulate content.

Determination of water (oil) binding capacity by modified clay samples

The LTM and LTM 011 samples were used for a study of their ability to adsorb water and oil depending on time. The obtained kinetic curves of water/oil sorption are presented in Fig. 8 and Fig. 9.

The water binding capacity of both the unmodified and the modified clay sample was conditioned by the presence of montmorillonite, characterised by the peculiar property of water molecule entry into crystal smectite lattice channels. It is seen (Fig. 8) 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.

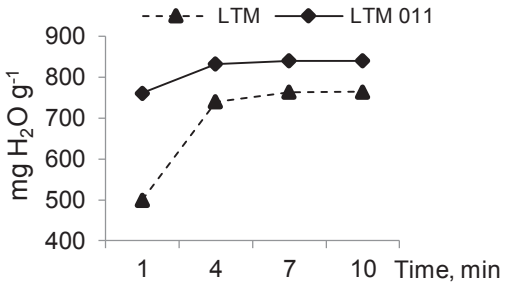

Figure 8. Water binding capacity of the control and modified clay samples depending on time.

Based on the data obtained (Fig. 9, a, b), 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.

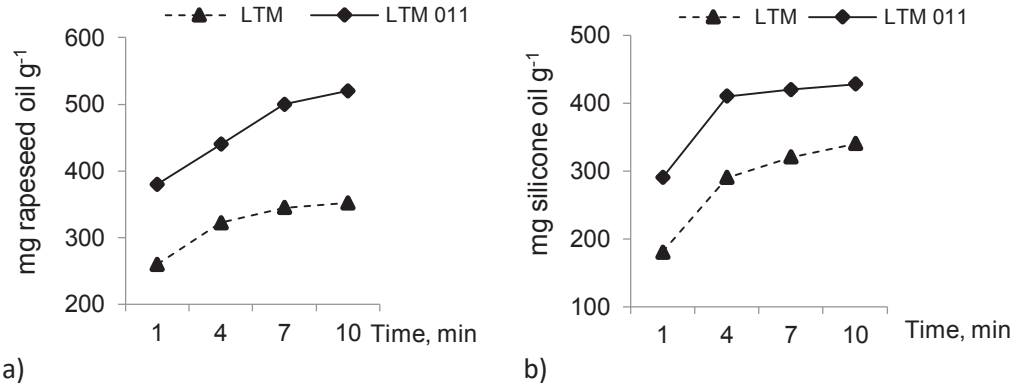

Figure 9. Rapeseed oil (a) and silicone oil (b) binding capacity of the control and modified clay samples depending on time.

To increase hydrophobicity of the clay samples, they were thermally treated at 800 °C. The oil binding capacity of the clay samples was studied for the LTM and the LTM 011 sample. It was found that 480 mg of silicone oil was absorbed by 1 gram of the LTM-800 sample, but for the sample LTM 011–800, this value was 640 mg per 1 gram. The sorption ability of rapeseed oil for the LTM and LTM 011–800 samples were 420 mg and 610 mg per 1 gram, respectively. The essential increase of the oil binding capacity for the LTM 011–800 sample was explained by its more hydrophobical

internal structure with higher pore sizes formed as a result of its thermal treatment compared with the structure of the thermally treated unmodified clay sample.

Determination of heavy metal ion sorption

As the conducted experiment shown, the LTM 800 and LTM 011–800 clay samples have tendency for metal ions sorption. After a 24–hour study, the concentration of zinc ions from water solution was reduced from 135 mg L^{-1} to 55 mg L^{-1} and 37 mg L^{-1} in presence of the LTM–800 and LTM 011–800 samples, respectively. Thus, the sorption efficiency was 60% and 72% for the unmodified and modified clay samples, respectively. It was found that the LTM 011–800 sample was a more effective sorbent for zinc ions than the unmodified clay.

Fig. 10 shows Freundlich adsorption isotherms for zinc adsorption by LTM 800 and LTM 011–800 clay samples.

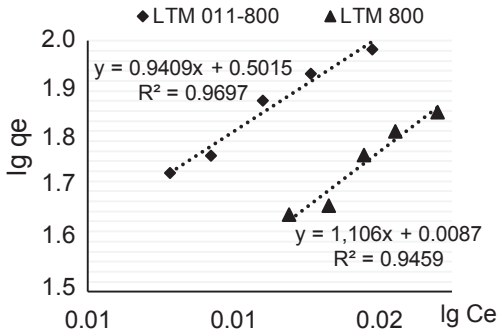

Figure 10. The Freundlich adsorption linear isotherm for Zn^{2+} ion adsorption by LTM 800 and LTM 011–800 clay samples.

Freundlich isotherm model parameters K_F and n for adsorbent LTM 011–800, calculated according to Eq. 4, are 3.17 for adsorption capacity and 1.06 for intensity of the adsorption. The correlation coefficient of Freundlich isotherm is 0.969 (Fig. 10). The present study results indicated that the Freundlich model fit the experimental data well. Freundlich isotherm model parameters K_F and n for adsorbent LTM 800 are 1.02 and 0.9 respectively. Larger value of n (smaller value of 1/n) implies a stronger interaction between the adsorbent and the adsorbate. If the value of n is between 1 and 10, it indicates a favorable adsorption Therefore, it can be concluded that, for the adsorption of Zn^{2+}, the modified clay sample is more powerful.

The same tendency was observed for Cu^{2+}. In summary, the recovery of Cu^{2+} from water solution by LTM 011–800 was 10% higher in comparison with the LTM 800.

CONCLUSIONS

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. The 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 with the new developed coagulant can be used to obtain of environmentally friendly and inexpensive clay-based sorbents.

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