

Feasible Technology for Agricultural Residues Utilization for the Obtaining of Value-Added Products

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ABSTRACT

The research is connected with the solving the problem of rational utilization of agricultural residues by the creation of resource-saving method for their efficient conversion into value-added products. Wheat straw was used in this work in chemical processing. Treatment was carried out with the application of formic/acetic acid mixture. Thus, cellulosic pulp was obtained. The spent solution was used to precipitate lignin. The structure of lignin was investigated. The results indicated that formic/acetic acid treatment was quite effective in isolating cellulose from wheat straw and in recovering lignin. Wheat cellulose is a promising fibrous material for the application in paper industry. Wheat lignin can be considered as a material for biosorbent preparation.

Keywords: wheat straw, acetic/formic acid, utilization, cellulose, lignin.

INTRODUCTION

Nowadays, a promising area of modern chemical technology is the development of resource-saving technologies with the application of agricultural and food residues (Bsoul et al. 2014; Kartel and Galysh, 2017; Gorobets and Karpenko 2017; Halysh et al. 2020). Today, millions of tons of grain are grown annually all over the world, resulting in formation of millions of tons of residues in the form of straw. Chemical processing of such residues allows obtaining cellulosic pulp that can be used in paper industry (Kamoga et al. 2013; Trembus et al. 2019). At the same time, this approach allows replacing expensive cellulose from wood in the composition of paper and cardboard (Trembus et al. 2018). The use of agricultural residues for cellulose production is connected with the creation of modern delignification

methods taking into account the requirements of reducing the emissions of harmful compounds into the environment.

Traditional sulfate and sulfite technologies of delignification are accompanied by the formation and emission of toxic sulfur-containing compounds. At the same time, the pollution of natural water with lignin-containing products also takes place. An important step in further development of the delignification technologies is the reducing of the harmful damage to the environment. One of the solutions is the development of new and modernization of existing technologies for cellulose production, e.g. organosolv delignification (Schulze et al. 2016; Salapa et al. 2017; Shui et al. 2018). Cellulose preparation from agricultural residues with the application of organic solvents is considered as a promising and eco-friendly method of delignification.

Solutions of aromatic and aliphatic alcohols, organic acids, ketones, ethers can be used as reagents in the delignification processes (Carvalho et al. 2015; Liao et al. 2020). Catalytic organosolv methods of delignification in acidic medium are quite perspective (Mamleeva et al. 2013; Deykun et al. 2018). The application of organic acids at the concentration of 4–10% ensures effective delignification at atmospheric pressure (Sarwar Jahan and Nayeem Rumme 2014; Halysh et al. 2018; Cheng et al. 2019).

Widespread use of acetic and formic as delignification reagents is connected with their strong ability to oxidase and to dissolve lignin. Both acids give cellulose with high yield due to the soft delignification and eliminate the further use of chlorine compounds for cellulose bleaching (Gong et al. 2016).

As a result of delignification, spent solutions are formed. Such spent solutions are rich in lignin, which is a promising material for production of chemicals and fuels (Zhang et al. 2018). Therefore, one of the current tasks is to study the composition and properties of cellulose and to study the possibility of lignin recovery from the spent solution.

The technologies of organosolv delignification are described in literature (Barbash et al. 2011), in contrast to the production of cellulose from wheat straw with the application of acetic/formic acid mixture.

Therefore, the purpose of the research work was to study the process of cellulose obtaining from wheat straw by formic/acetic acid delignification as well as the lignin recovery from the spent delignifying solution.

MATERIALS AND METHODS

Wheat straw (*Triticum vulgare*) was used for cellulose production. The straw was sorted from grass and from knots. The chemical composition of initial material was determined in accordance with TAPPI standards (Halysh et al. 2019). The chemical composition was as follows, %: cellulose – 45.6, lignin – 17.1, solubility in hot water – 10.6, solubility in NaOH – 37.2, resins, fats and waxes – 5.4, ash – 6.9.

Wheat straw was treated with a mixture of acetic (CH_3COOH) and formic acid (HCOOH) at a different ratio and the concentrations of the acids were 60 and 40%, respectively. Treatment

was conducted in glass flasks at a solid to liquid ratio 1:10, at a temperature 90 ± 2 °C and during 180 min. The yield of cellulose was determined gravimetrically. The values of selectivity, degree of delignification, degree of carbohydrate removal were calculated as described in (Barbash et al. 2014).

In order to evaluate the feasibility of lignin recovery, the spent solution after wheat straw treatment was collected into a flask and left in a dark place at room temperature for 24 h, then filtered through a glass filter (pore grade – G3). Then, lignin was dried in air to a moisture content of 7%.

The infrared (IR) spectroscopy and scanning electron microscopy (SEM) methods were used to determine the structure of lignin. The IR spectrum of lignin was recorded on a Specord M80 spectrophotometer (Carl Zeiss, Germany) in the range of 300–4000 cm^{-1} . SEM of the sample surface structure was performed using a JEOL JSM-5500LV microscope equipped with an EDS/EDX/EDAX and ESEM analyzer (JEOL Ltd., Japan). The total pore volume of lignin was determined by using the method of benzene vapor absorption in the desiccator.

The effect of pH on the sorption efficiency of cationic dye was studied using model solutions of methylene blue. The lignin sample mass was 0.2 g, and the volume of the dye solution (concentration of 100 mg/l) was 50 ml, sorption period was 240 minutes. Solutions of 0.1 N hydrochloric acid and 0.1 N sodium hydroxide were used to achieve the pH. The starting and equilibrium concentrations of dye were determined spectrophotometrically at a wavelength of 664 nm.

The sorption capacity of lignin towards dye was calculated by the formula:

$$q = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where: C_0 and C_e – the initial and equilibrium concentrations, respectively (mg/l);

V – the volume of the model solution (ml); m – the mass of sorbent (g).

A model solution of methylene blue with a neutral pH was used to study the sorption kinetics. Kinetics studies were performed during 8 hours. For a detailed description of the sorption kinetics, models of pseudo-first order, pseudo-second order and intramolecular diffusion were selected and their linear forms are the following:

$$\ln(q_e - q_t) = \ln q_e - \frac{k_1 t}{2.303} \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}, \quad (3)$$

$$q_t = k_3 t^{1/2} + C, \quad (4)$$

where: q_p and q_t – the amount of sorbed dye at equilibrium and in time t (min), respectively (mg/g); k_1 – the rate constant of the pseudo-first order model (min^{-1}); k_2 – the rate constant of the pseudo-second order model (mg/g·min); k_3 – the rate constant of the intramolecular diffusion model (mg/g·min^{1/2}); C – the thickness of the layer (mg/g).

The studies of the effect of dye concentration on the efficiency of its removal were performed using 0.2 g of lignin and a volume of model solution (dye concentration 30–900 mg/l) 50 ml, the process time was 240 min. The Langmuir and Freundlich isotherms were used to study the mechanism of sorption in details:

$$\frac{C_e}{q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m}, \quad (5)$$

$$\log q_e = \log K_F + \frac{\log C_e}{n}, \quad (6)$$

where: C_e – the equilibrium concentration of dye (mg/l); q_e – the amount of sorbate per unit mass of sorbent (mg/g); Q_m – maximum adsorption capacity (mg/g); K_L – the constant of the Langmuir equation (l/mg); K_F – the constant of the Freundlich equation (l/g); n – the empirical constant.

RESULTS AND DISCUSSION

In order to investigate the efficiency of wheat straw treatment with formic/acetic acid mixture

onto cellulose yield, lignin content, degree of delignification, selectivity and degree of carbohydrates removal, the process was carried out at different ratio of acids (Fig. 1).

The obtained results (Fig. 1) show that increasing the content of formic acid in the mixture of organic acids leads to the decrease in the cellulose yield and in the content of residual lignin due to the acidolysis and fragmentation of lignin macromolecule, the cleavage of lignin-carbohydrate bonds, oxidation and dissolution of hemicelluloses.

It is obvious that at the ratio HCOOH:CH₃COOH of 80:20 vol.% the content of lignin in the final cellulosic product decreases quite significantly and the cellulose yield decreases significant too. This is the evidence of the destruction of the carbohydrates in wheat straw during treatment. Therefore, the process of treatment of wheat straw should be carried out at a HCOOH:CH₃COOH ratio of no more than 70:30 vol.%. As it can be seen from Fig. 1, the optimal values of selectivity, degree of delignification, degree of carbohydrate removal of the final product after wheat straw delignification process were achieved for the ratio of HCOOH to CH₃COOH 70:30 vol.%.

The feasibility of any chemical technology depends on the efficiency of by-products utilization. Spent solutions after treatment of biomass with any delignifying solution are enriched with lignin which is a promising material for further processing into valuable chemicals and fuels. In view of this, it is necessary to study the possibility of lignin recovery and investigate its properties. For this purpose, the spent solution after wheat straw treatment with formic/acetic acid mixture at the

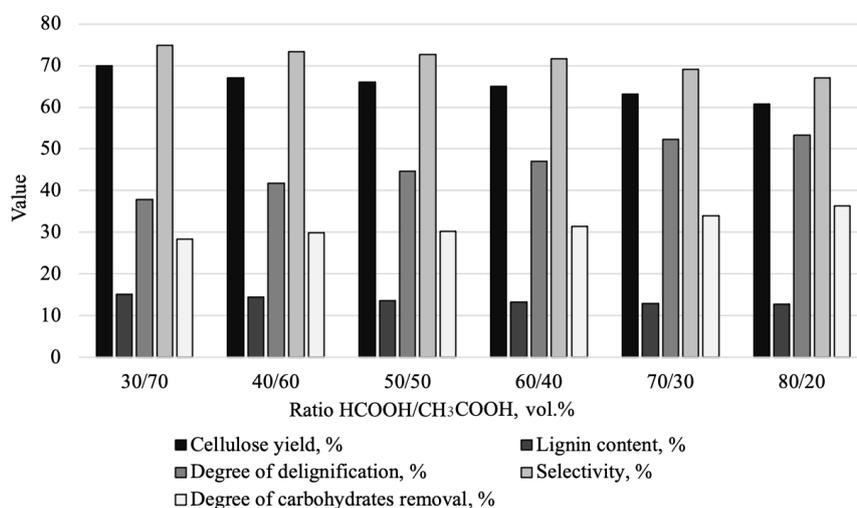


Fig. 1. Effect of formic/acetic acid ratio in mixture onto the efficiency of wheat straw treatment

ratio of acids 70:30 vol.%, respectively, was used. Lignin was precipitated and separated by filtering, as described above.

The IR spectrum of lignin is shown in Fig. 2. The wide band in the range of 3410–3460 cm^{-1} belongs to hydroxyl groups in phenolic and aliphatic structures of lignin units. The absorption bands at 2910 cm^{-1} and at 2853 cm^{-1} appear mainly from the vibrational oscillations of the methoxyl groups of the aromatic rings in lignin, as well as the methyl and methylene groups of the side aliphatic chains of phenylpropane structural units. The presence of a band at 1702 cm^{-1} associated with the presence of carbonyl or carboxyl groups in sample. Intense absorption bands at 1648, 1532 and 1463 cm^{-1} belong to the aromatic structures of lignin. The peaks at 1324, 1211 and 1117 cm^{-1} are characteristic for oscillations of syringyl and guaiacyl rings of lignin units. The peak at 1037 cm^{-1} is characteristic of the oscillations of the C-H, and the bands at 1099 and 1022 cm^{-1} correspond to the C-O bond of polysaccharides. The absorption band at 835 cm^{-1} corresponds to the deformation oscillations of C-H bonds in aromatic rings (Sammons et al. 2013; Dörstein et al. 2018). The IR spectrum indicates that the studied sample contains a small amount of components of the polysaccharide nature.

The surface of lignin (Fig. 3) is represented by diverse particles of different shapes, which have a wide range of sizes. It is characteristic for

precipitated lignins (Köhnke et al. 2019). Most particles have a smooth surface, which indicates a low porosity of the studied material.

The results of benzene vapors sorption showed that the value of the volume of adsorption pores for the lignin is 430 mm^3/g (Table 1). The bulk and true density of the lignin are 0.43 and 0.84 g/cm^3 , respectively. The value of specific surface area indicate a good possibility for the application of lignin as a biosorbent for wastewater treatment.

The sorption of methylene blue was studied to evaluate the possibility of lignin application for the purpose of sorption. Biosorption is a promising technique in wastewater treatment with the application of biomass or its structural components for different pollutants removal (Conrad et al. 2014; Gupta et al. 2015; Halysh et al. 2020). This approach will simplify water treatment technology and eliminate the need for costly reagents (Trus et al. 2019; Radovenchyk et al. 2021).

The sorption efficiency of cationic dye depends on the pH of its solution due to the property of the surface of lignocellulosic materials to acquire the positive, neutral or negative charge in solutions depending on the pH (Fathy et al. 2013). As it can be seen from Fig. 4, the efficiency of methylene blue absorption onto lignin greatly depends on the pH of the model solution. Sorption capacity increases quickly from 20.2 mg/g to 31.5 mg/g with the increase of pH in

Table 1. The surface characteristics and densities of the lignin

Parameters	Adsorption pore volume, mm^3/g	Bulk density, g/cm^3	True density, g/cm^3	S_{BET} , m^2/g	Pores volume, mm^3/g	Micropore volume, mm^3/g
Values	430	0.43	0.84	280	140	120

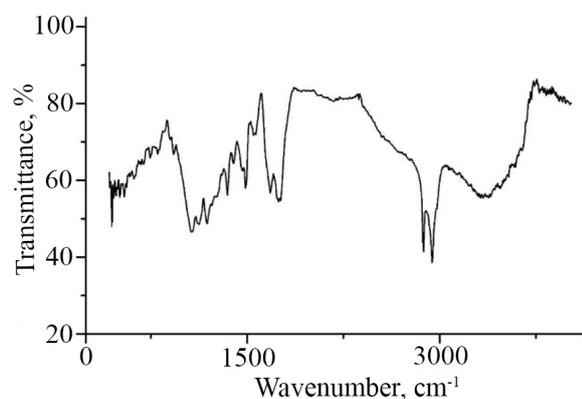


Fig. 2. IR spectrum of lignin from wheat straw

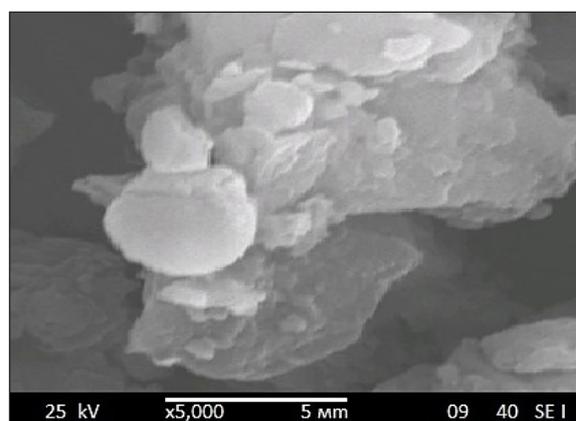


Fig. 3. SEM image of lignin from wheat straw

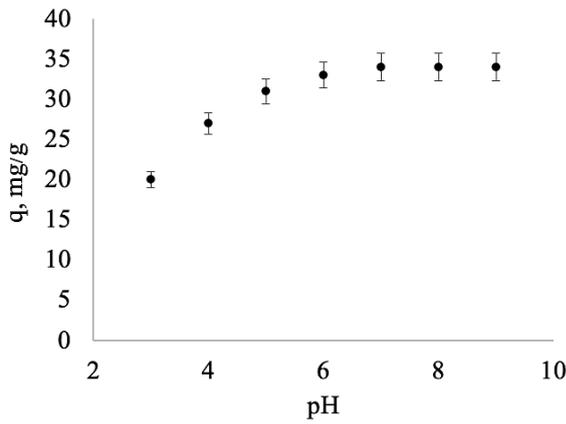


Fig. 4. Influence of pH on the sorption capacity of lignin

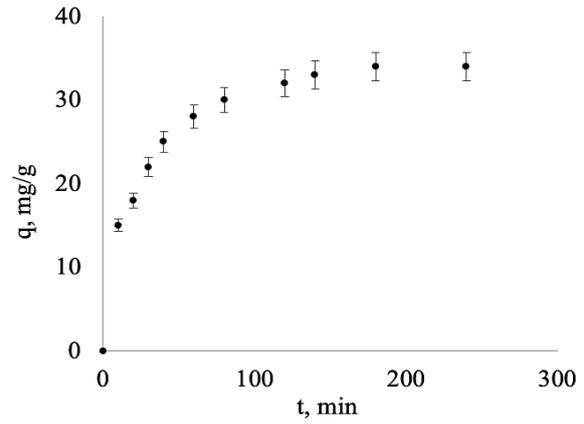


Fig. 5. Dependence of the sorption capacity of lignin on the time of the process

the range from 3.0 to 5.0. The next change in pH is slightly smaller, affecting the sorption efficiency and the maximum capacity (34.0 mg/g) is reached at pH 6 and stays constant with the further increase in pH. Lignin is known to contain phenolic and aliphatic hydroxyls that can be easily protonated and deprotonated at different pH values. This fact is associated with the high sorption ability of the studied material at higher pH values, as the lignin surface acquires a negative charge. Probably, the interaction between positively charged dye cations and negatively charged lignin surface is electrostatic. In the case of lignocellulosic materials, the fixation of cationic dyes on their surface is possible with the involvement of chemical and physical bonding mechanisms (Liu et al. 2015).

The dependence of the sorption of methylene blue onto lignin on the time of the process is given in Figure 5. It is seen that during the first 60 min of contact, there is a maximum absorption of dye is observed, but the next sorption is a little bit slower and complete equilibrium occurs within 120 min from the beginning of the experiment.

Table 2. Parameters of kinetic models of the sorption process of methylene blue onto lignin

Kinetic model	Parameters	Values
Pseudo-first-order	k_1, min^{-1}	0.02
	$q_e, \text{mg/g}$	25.7
	R^2	0.9849
Pseudo-second-order	$k_2, \text{mg/g}\cdot\text{min}$	0.001
	$q_e, \text{vg/g}$	37.0
	R^2	0.9992
Intraparticle diffusion	$k_3, \text{mg/g}\cdot\text{min}^{1/2}$	2.07
	C	8.15
	R^2	0.8562

The study of adsorption kinetics is important, because it provides the information about the mechanism of the pollutant absorption. For this purpose, models of pseudo-first and pseudo-second order, as well as intramolecular diffusion were used. Kinetic models of sorption of methylene blue on lignin in linear form are presented in Figure 5, and the values of the calculated coefficients of the kinetic models are summarized in Table 2.

The adsorption isotherm plays an important role in describing how the adsorbate interacts with the sorbent and gives an idea of the adsorption capacity of the material. As it can be seen, at the initial concentration of methylene blue in a solution below 100 mg/l, the sorption capacity increases linearly along with the concentrations (Fig. 6). Then, the increase in sorption capacity is slower to a maximum of 44.7 mg/g.

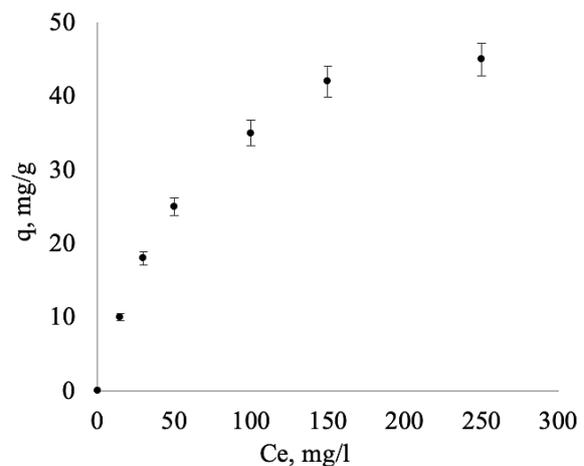


Fig. 6. Dependence of lignin sorption capacity on equilibrium dye concentration

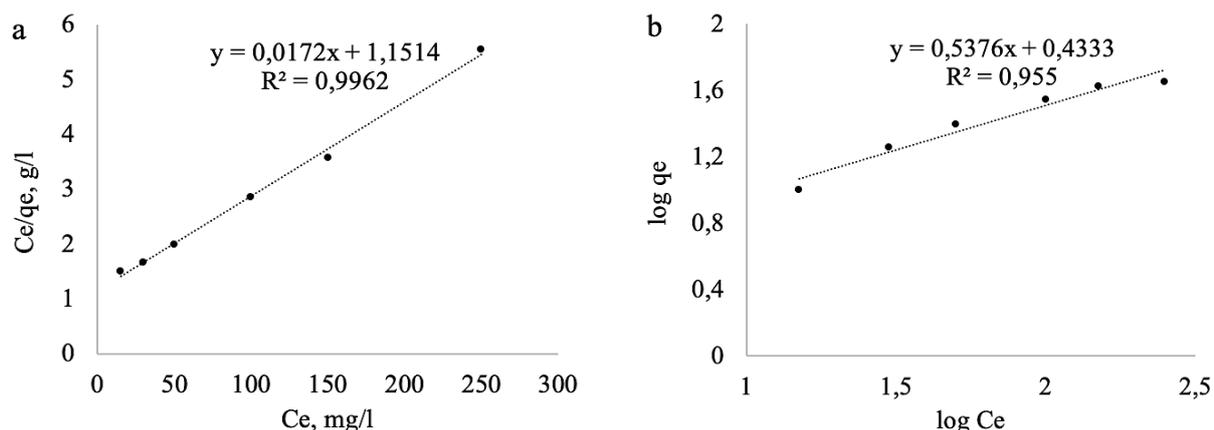


Fig. 7. Langmuir (a) and Freundlich (b) isotherms of methylene blue sorption onto lignin

The Langmuir and Freundlich isotherms were used to establish the mechanism of interaction of the adsorbate with the sorbent. The Langmuir isotherm describes monolayer adsorption on a homogeneous surface, while the Freundlich isotherm describes an imperfect multilayer adsorption on inhomogeneous surfaces. The linear forms of both isotherms of dye adsorption on lignin are presented in Figure 7, and the values of the coefficients of the respective models are given in Table 3.

Table 3. Parameters of the Langmuir and Freundlich isotherms of methylene blue sorption onto lignin

Sorption isotherms	Parameters	Values
Langmuir	K_L , mg/l	0.015
	Q_m , mg/l	58.1
	R^2	0.9962
Freundlich	K_F , l/g	2.71
	n	1.86
	R^2	0.955

The equilibrium model, which best describes the sorption process, is established by the value of the correlation coefficients of linear regression (R^2). Compared with the Freundlich equation ($R^2 = 0.955$), the Langmuir equation ($R^2 = 0.9962$) is the most suitable for describing sorption and shows that adsorption sites on the lignin surface are homogeneous and cationic dye adsorption is monolayer.

In general, the presented results correlate well with the literature data. In addition, it was found that lignin from wheat straw has a sorption capacity slightly higher than lignin from rice straw (Zhang et al. 2016).

CONCLUSIONS

The feasibility of wheat straw chemical treatment with the application of formic/acetic acid mixture was studied. Cellulose of high quality with the yield in the range of 60.8 to 70.0% and with the content of lignin from 15.2 to 12.8% was obtained. It was shown that wheat straw treatment with $\text{HCOOH}:\text{CH}_3\text{COOH}$ mixture at a ratio of 70:30 vol.% allows obtaining cellulose with optimal selectivity, degree of delignification, degree of carbohydrate removal. Lignin was obtained as a by-product. The structural properties of lignin were characterized and sorption properties of lignin in respect to methylene blue were studied. It was shown that the specific surface area of lignin was $280 \text{ m}^2/\text{g}$. The results also indicate that the lignin from wheat straw can be a potential sorbent for cationic dyes removal from water solutions.

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