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The Possibility of Using Waste from Dye Sorption for Methane Production

Anna Nowicka , Tomasz Jóźwiak and Marcin Zieliński *

Department of Environmental Engineering, Faculty of Geoengineering, University of Warmia and Mazury in Olsztyn, 10-720 Olsztyn, Poland; anna.grala@uwm.edu.pl (A.N.); tomasz.jozwiak@uwm.edu.pl (T.J.)
* Correspondence: marcin.zielinski@uwm.edu.pl; Tel.: +48-89-523-4124

Abstract: The aim of this study was to determine the effect of sorption of Basic Red 46 (BR46) dye by lignocellulosic biomass on the susceptibility of the sorbed waste to anaerobic decomposition by anaerobic digestion. The research material used in the experiment consisted of two types of biomass: stalks with leaves and inflorescences after mowing Canadian goldenrod (*Solidago canadensis* L.) (GB), and rapeseed hulls (RHs) after oil pressing. During the anaerobic decomposition of RHs, 732.30 NmL/gVS and 646.63 NmL/gVS of methane were obtained from the non-sorbed substrate and the plant material after dye sorption, respectively. Similarly, in the variants using Canadian goldenrod, the production was 220.70 NmL/gVS and 183.20 NmL/gVS. The GB sorbent sorbed 34% more BR46 dye than the RH sorbent, which is likely to have resulted in the accumulation of VFA and contributed to the partial inhibition of methane production. In light of the obtained results and the literature data, it is concluded that there is a possibility of effective use of dye sorption waste for methane production.

Keywords: anaerobic digestion; methane; waste; dye sorption

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1. Introduction

Conventional fuels are currently the most popular energy carriers in the world. Oil, coal, and natural gas are the most widely used energy sources, providing about 83% of total energy demand. However, it should be borne in mind that the aforementioned raw materials are nonrenewable and their resources are exhaustible, so the existing deposits of energy raw materials may prove insufficient [1].

Existing problems with the availability of raw materials due to the depletion of nonrenewable fuel resources as well as energy and geopolitical crises negatively affect the prices of conventional energy sources. The cost of fossil fuel imports to Poland in 2022 was PLN 193 billion, 91 billion more than in 2021. The price of atmospheric CO_2 emission allowances has increased several times in recent years and averaged EUR 86 per ton in 2022, while in 2018, it was less than EUR 10. Currently, 48% of Polish emissions are covered by the EU Emissions Trading Scheme—EU ETS [2].

The answer to the emerging problems is alternative energy sources, which include solar, hydroelectric, geothermal, nuclear, wind, and biofuel energy, among others [3]. Renewable energy production (RES) has increased by 117% over the past decade, yielding 36.8 TWh of energy from renewable sources in 2022. RES accounted for 20.6% of the generation mix in 2022, with 3.2% of energy coming from biomass and biogas plants [2].

Lignocellulosic biomass represents a vast untapped energy source. It can only be considered as an attractive alternative to fossil fuels if it is produced and processed without negative environmental impacts. Of the many biological technologies, anaerobic digestion is the most cost-effective and is widely used for the commercial production of renewable energy from lignocellulosic biomass. The direct use of lignocellulosic biomass for biogas production via anaerobic digestion is limited due to the structure of the lignocellulosic complex, which makes it resistant to fermentation [4]. Due to the many factors limiting the biodegradation process of lignocellulosic material, it must be pretreated. Effective pretreatment should ensure separation of lignin from cellulose, highly amorphous cellulose content, high substrate porosity, no sugar losses, reduced inhibitor production, and low energy input. Common conditioning techniques can be divided into physical, physicochemical, chemical, and biological [5].

The substrate for anaerobic digestion, which produces biomethane, can be any type of biomass, the main components of which are carbohydrates, proteins, fats, cellulose, and hemicellulose. This means that a great many products of organic origin can take part in the biogas production process. Very often as a substrate for anaerobic digestion, agricultural waste, organic waste from landfills, or sewage sludge is used [6].

The efficiency of conversion to biofuels is determined by the amount of dry matter and calorific value. Typically, lignocellulosic biomass contains about 20% water, the rest is mainly organic matter, and the mineral part is a small proportion (Figure 1). The content of a given component in a plant is mainly determined by its species, age, or growth stage. Determining the structure of the plant, i.e., determining the relative amounts of cellulose, hemicellulose, and lignin, is important in order to appropriately choose how to convert the energy contained in a given type of biomass [7]. Lignocellulose, which is a combination of cellulose, hemicellulose, and lignin, is contained in almost half of the plant substances produced by photosynthesis. Unfortunately, only insignificant amounts of lignocellulosic raw materials, which are by-products of agricultural and forestry management, are used, and the rest is lost as waste. Cellulose contributes the largest share of the structure of lignocellulose, followed by hemicellulose and lignin. Depending on the plant, the composition and proportions of the compounds vary. Table 1 shows the proportions of lignocellulosic components in selected substances [8]. With the growing interest in biogas production, the amount of feedstock used in anaerobic digestion is increasing. Precipitation from dye sorption may become such a feedstock. Nowadays, waste materials based on plant biomass, mainly waste from the agrifood industry, are becoming increasingly popular sorbents. Through its low price and availability in most countries around the world, plant-based precipitation is becoming a competitor among the materials most readily used as sorbents [9].

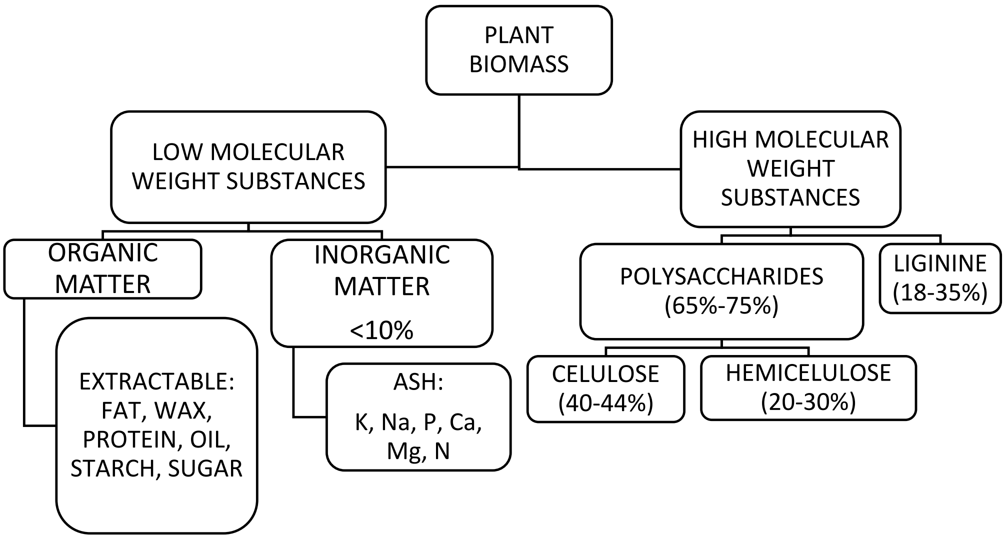


Figure 1. Chemical composition of plant biomass [10].

Table 1. Characteristics of native materials.

Parameter [Unit]	GB	RH
Total solids [mg/g]	977.5 ± 24.51	929.4 ± 31.90
Mineral solids[mg/g]	48.9 ± 3.23	48.7 ± 2.82
Voiataile solids [mg/g]	928.6 ± 36.17	880 ± 29.26
Lignin [%]	10.19 ± 0.78	8.52 ± 0.57
Cellulose [%]	37.09 ± 3.02	15.24 ± 1.19
Hemicellulose [%]	5.22 ± 0.43	2.91 ± 0.28

The textile, tanning, and paper industries are producers of wastewater with a high content of dyes, usually of synthetic origin. Problems with their biodegradability are most often due to their complex chemical structure and high durability [11]. When colored substances enter aquatic ecosystems, there is a risk of adverse effects [12]. The most dangerous of these is the restriction of access to solar radiation for autotrophic organisms, which is a problem for primary production near sources of pollution in reservoirs [13]. Colored substances can have the effect of reducing the diffusion of atmospheric oxygen in the water, which, along with a decrease in the photosynthesis of hydrophytes, can lead to anaerobic conditions, posing a serious threat to entire aquatic ecosystems [14]. In order to protect the environment, it is necessary to use techniques that can clean up colored industrial wastewater as much as possible.

Wastewater decolorization methods that degrade the environment to a small extent include sorption, which is not accompanied by the production of sludge and toxic intermediate products. The course of the process is relatively simple, and the cost depends on the substance used for sorption. To date, the most commonly used sorbents have been materials made of activated carbons. Due to their low availability and relatively high price, alternative, cheaper substitutes are being sought [15]. As an alternative, waste materials from the agricultural and food industries are becoming available for use in the production of sorption materials. For this purpose, the stems and leaves of crops and the seed husks or peels of vegetables and fruits can be used [9]. Sorbents based on the aforementioned plants perform well in removing alkaline dyes, thanks to their specific chemical structure, influenced by the presence of polysaccharides and lignins [16]. In addition to agricultural waste, invasive plants are a source of cheap and readily available biomass [17].

Currently, used biosorbents very often end up in landfills [18]. The disadvantage is that the dyes present in the sorbents can be washed away over time and contaminate local soils or ground and surface water. Another possibility for the utilization of spent plant-based sorbents could be their carbonization and activation to produce full-value activated carbons [19]. However, this process would be quite energy-intensive and the quantities of product obtained would be relatively small. Given the high calorific value of both plant biomass and the dyes themselves, a more favourable way of managing used biosorbents could be to dry them and then co-fire them in a combined heat and power plant to generate thermal energy [20].

A weakness of the combustion of dye-containing materials is the high risk of harmful emissions into the atmosphere, especially if the combustion temperature in the boiler is <850 °C. An alternative way to recover the chemical energy contained in spent lignocellulosic biosorbents could be to ferment them to produce methane. The main obstacle to this type of solution could be the detrimental effect of the dyes contained in the sorbents on the functioning of the methanogens.

The purpose of this study was to determine the susceptibility of lignocellulosic waste from Basic Red 46 (BR 46) dye sorption to anaerobic decomposition in methane digestion, and to investigate the effect of dye sorption by lignocellulosic material on methane production from this material.

2. Materials and Methods

2.1. Research Scheme

The research was divided into 5 parts; the diagram shows a detailed research plan (Figure 2).

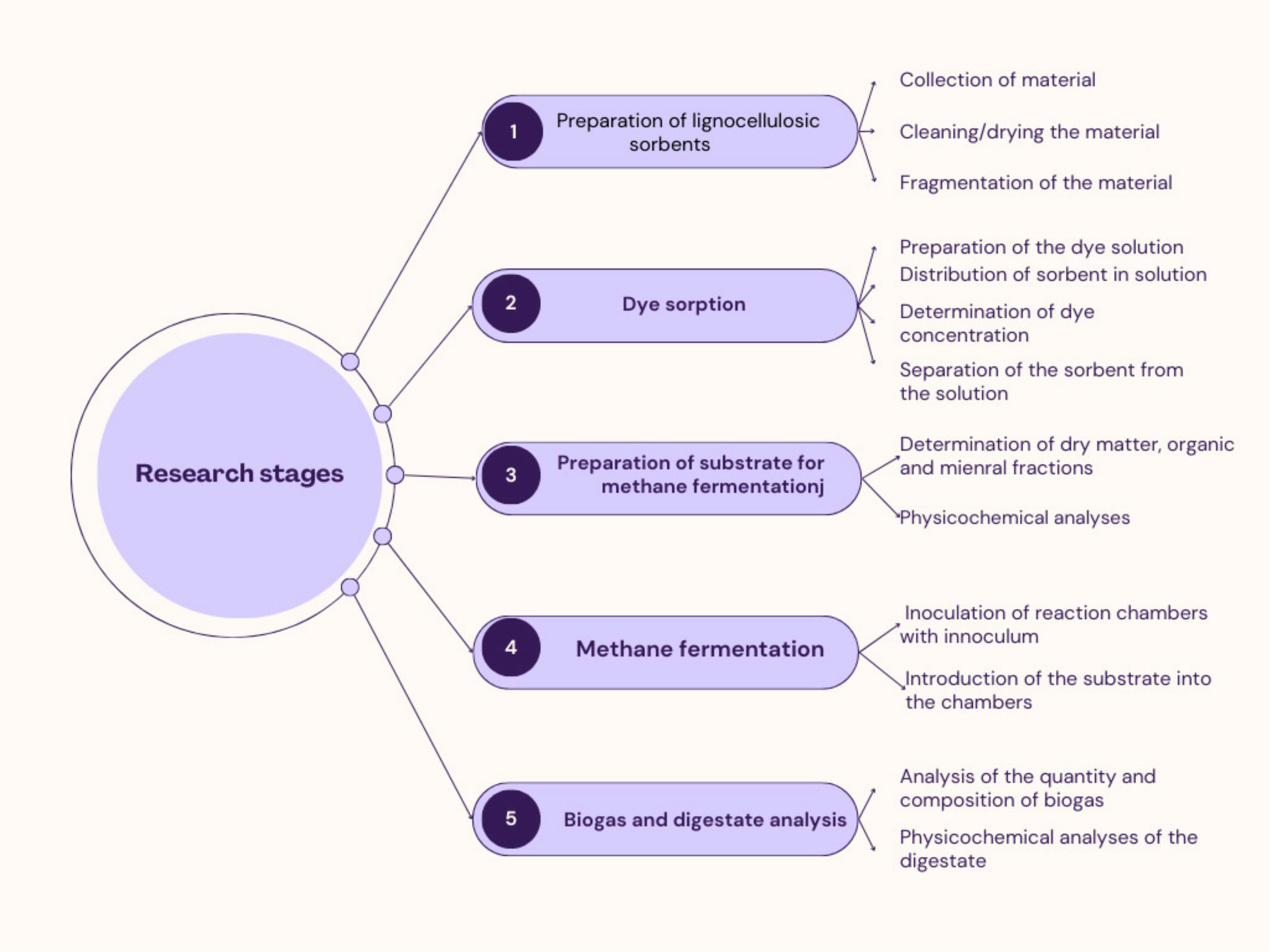


Figure 2. Experiment plan.

2.2. Raw Materials for the Production of Lignocellulosic Sorbents

Canadian goldenrod biomass (GB) included stems with leaves and inflorescences of Canadian goldenrod (*Solidago canadensis* L.), which was mowed in August 2022 in a meadow in the Warmińsko–Mazurskie province (Poland).

Rapeseed husks (RHs) were processed using an oil extruder located in the Warmian–Masurian province (Poland). The raw material came from industrial rapeseed (*Brassica napus* L.) from a local harvest conducted in the first half of August 2022. Preparation of the sorbent for testing consisted of separating the rapeseed hulls from the oil cake containing the crushed seed kernel. This procedure is described in more detail below.

Before sorption in the substrates, the dry matter content, organic, and mineral fraction content of the substrates were determined in accordance with the Polish Standard (PN-C-04541:1978). The contents of cellulose, hemicellulose, and lignin were also determined using the method proposed by van Soest et al. [21]. A semi-automatic ANKOM220 fiber analyzer was used to perform chemical fractionation using detergents. The method analyzed the compactness of the fiber fractions including neutral detergent fiber (NDF), acid detergent fiber (ADF), and acid detergent lignin (ADL) (Table 1).

Basic Red 46 (BR46) cationic dye was purchased from the "BORUTA S.A." dye manufacturing plant in Zgierz (Łódz province, Poland). BR46 is a typical basic dye. It belongs to the class of azo dyes ("single azo dye") and contains a quaternary ammonium cation in its structure, which gives it an alkaline character (Figure 3). It has a molar mass of 401.3 g/mol, and its molecular formula is C18H21BRN6. It shows an absorption maximum (λmax) at 530 nm. BR46 is used for dyeing leather, wool, cotton, paper, acrylic fibers, and also as an additive in printing inks and hair dyes. It has corrosive properties. It exhibits toxic effects on aquatic organisms. The manufacturer's declared content of pure BR46 in the commercial product is 80%. Its popular trade names include Anilan Red GRL, Basic Red X-GRL, and Kationic Red X-GRL.

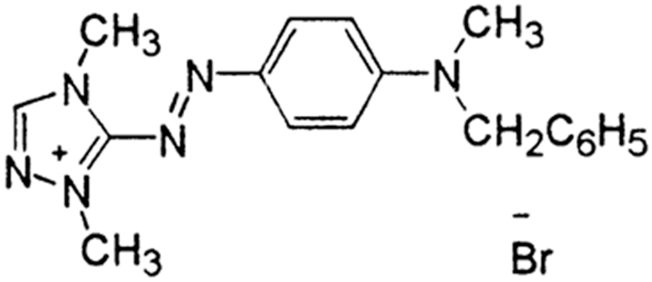


Figure 3. Chemical structure of Basic Red 46 (BR46) dye.

2.3. Preparation of Sorbents

For preparation of sorbent based on GB (GB–S), stems of Canadian goldenrod with leaves and inflorescences were rinsed with deionized water to remove impurities. The biomass was then dried in a laboratory dryer (105 °C), followed by grinding in a Microfine MF-2 laboratory grinder (CONBEST, Kraków, Poland). The ground biomass was passed through a laboratory sieve with a mesh diameter of 3 mm and then through a sieve with a mesh diameter of 2 mm. The biomass fraction with a diameter of 2–3 mm was washed with deionized water. The resulting material (GB–S) was ready for sorption after redrying (105 °C) (Figure 4).

Figure 4. Prepared sorbents, from **left**: Canadian goldenrod (GB), **right**: rapeseed hulls (RHs).

For preparation of RH-based sorbent (RH–S), the rapeseed husks were placed in a laboratory beaker (5 L), and 3 L of deionized water heated to 50–55 °C was then added to the beaker. The contents of the beaker were stirred vigorously with a spatula for 5 min. The stirring speed ensured that the rapeseed cake was evenly distributed throughout the solution. While stirring, the crushed rapeseed kernels separated from the hulls. The contents of the beaker were then poured through a sieve with a mesh diameter of 0.5 mm.

This mesh diameter ensured that the rapeseed hulls were retained on the sieve and at the same time allowed the crushed seed kernel fragments to pass through. The rapeseed hulls that remained behind the sieve were reintroduced into the beaker to repeat the process of separating the seed kernels from the hulls. The described process was repeated several times until the hulls were completely cleaned of the remaining crushed seed kernels (until the water used for washing the hulls was completely clear). The cleaned rapeseed husks (RH–S) were ready for sorption after drying (Figure 4).

2.4. BR46 Sorption

Into a laboratory beaker (1000 mL), 40 g DM of sorbent was weighed on a precision balance. Then, 800 mL of BR46 solution with a concentration of 10,000 mg/L and pH 6 was added to the beaker. The optimum pH for sorption of the dye (pH6), determined from preliminary tests, was used during the process. The beaker was placed on an MS-53M multi-station magnetic stirrer (JEIO TECH, Daejeon, Republic of Korea) set at 200 r.p.m. Mixing was carried out with a Teflon-coated magnetic stirrer measuring 8 × 50 mm. The temperature of the solution during sorption was 25 °C. The stirring conditions ensured even distribution of the sorbent throughout the solution. After 12 h of sorption, the assumed sorption time allowed the system to reach sorption equilibrium. Solution samples were taken from the beakers for spectrophotometric determination of the concentration of dye remaining in the solution. The sorbent with the sorbed dye was separated from the solution on a laboratory sieve with a mesh diameter of 0.5 mm. To speed up the removal of residual dye solution from the sorbents, the laboratory sieve with the sorbent was then placed on absorbent paper towels. For each sorbent, BR46 sorption was carried out in triplicate (a total of 6 test runs). The sorbents with sorbed dyes were not dried before testing for their susceptibility to anaerobic digestion.

2.5. Physicochemical Analyses of Sorbents after Dye Sorption

Before the methane digestion process, the total solids, mineral solids, and volatile solids of sorbents with sorbed dyes were determined [22]. The prepared samples were also subjected to chemical analysis. Before the analysis was conducted, the substance was properly prepared. After mixing the biomass with inoculum—anaerobic sludge from an agricultural biogas plant—the test material was shaken, using an IKA 4000 shaker and control (IKA, Karnataka, India). The machine was operated at 130 rpm for 60 min. Then, the prepared samples were placed in an Eppendorf Centrifuge 5804R (EPPENDORF, Hamburg, Germany); the centrifugation time was 3 min and the speed was 11,000 rpm. Thanks to the performed steps and with the use of filter membranes with a pore size of 1.2 µm according to the method by Hach (LCK 904), the liquid fraction was separated from the solid substance.

Obtaining the liquid fraction of the substrates allowed analysis of chemical oxygen demand COD according to the method by Hach (LCK 014). The tests used bar-coded 13 mm vials for chemical oxygen demand analysis. With automatic test recognition (on compatible systems), they analyzed the COD concentration after adding the correct amount of sample to the vial and mineralizing. The results are displayed as O_2 mg/L. A 13 mm reactor was required for sample digestion, compatible with HT200S for rapid COD digestion. A suitable photometer or spectrophotometer was required for analysis; the results were read on a Hach Lange DR 5000 spectrophotometer (HACH, Loveland, CO, USA).

The concentrations of five- and six-carbon sugars (glucose and xylose) in the filtrate were also checked using assay kit tests from Megazyme (MEGAZYME, Bray, Ireland).

For quantitative determination of elemental percentages, the Flash 2000 Elemental Analyzer (Thermo Fisher Scientific, Waltham, MA, USA) was used, with which nitrogen, carbon, and hydrogen contents of solid samples were determined.

Analysis of organic carbon TOC, total carbon TC, inorganic carbon IC, and total nitrogen TN in the samples after membrane filtration was performed using a Shimadzu TOC analyzer (Shimdzu, Kyoto, Japan).

2.6. Anaerobic Digestion

Testing of the substrate's susceptibility to anaerobic decomposition under anaerobic digestion conditions was carried out using an AMPTS II Bioprocess Control Automatic Methane Generation Potential Tester (BPC Instruments AB, Mobilvägen, Sweden). The system consisted of three subunits. The main component included bioreactors placed in a water bath that allowed the system to maintain a constant temperature. Bioreactors with a volume of 500 mL were used in this study. The reaction chambers were connected to stepper motors, allowing the contents of the reactors to be mixed with slow rotary stirrers. Mixing was carried out cyclically every 10 min for 30 s at a speed of 100 rpm. The biogas from the reaction chambers went into scrubbers containing a NaOH solution, and in this part of the system, the acidic components of the biogas, such as CO_2, were absorbed. In contrast, the CH_4 contained in the samples passed into the detection unit. Another component was a methane microfluidic measurement system, which consisted of a water tank with measurement cells with motion sensors placed inside. Each reaction chamber corresponded to one measuring cell, which enabled fully automatic measurement of the amount of biogas produced, thanks to the built-in motion sensors. The device measured the volume of methane produced by measuring the number of openings of measuring cells of known capacity (measurement resolution of 10 mL). The quality of the biogas produced was measured by taking samples from the reaction chamber and analyzing them using a 7890A GC gas chromatograph with a TCD detector (Agilent Technologies, Santa Clara, CA, USA).

In each of the conducted variants of the experiment, the reaction chambers were inoculated with anaerobic sludge from an agricultural biogas plant. An initial load of organic compounds of 5.0 kg VS/m^3 was applied.

Two substrates were subjected to anaerobic digestion, each in two variants, after sorption: GB–S and RH–S, and substrate not subjected to GB and RH sorption. Each variant tested was subjected to fermentation in triplicate, and the results obtained and described included the average values of those obtained for a single variant.

After the digestion process, determinations similar to those in Section 2.5 were made for the digested samples.

2.7. Calculation Methods

The content of structural cell wall polymers was calculated based on Equations (1)–(3):

$$Cellulose = ADF - ADL \tag{1}$$

$$Hemicellulose = NDF - ADF \tag{2}$$

$$Lignin = ADL \tag{3}$$

The amount of dye adsorbed on tested sorbents was determined from Formula (4):

$$Qs = (C_0 - C_S) \times \frac{V}{m} \tag{4}$$

where Q_S is the mass of sorbed dye [mg/g], C_0 is the initial concentration of the dye [mg/L], C_S is the concentration of the dye after sorption [mg/L], V is the volume of the solution [L], and m is the mass of the sorbent [g].

As anaerobic digestion most closely fits first-order kinetics, methane production can be described by the following Equation (5):

$$C = C_e \times \left(1 - e^{k \cdot t}\right) \tag{5}$$

where C is the cumulative biogas yield (NmL/g VS) in the fermentation time t, C_e is the maximum biogas yield (NmL/g VS), and k is the kinetic biogas production factor (d^{-1}).

The values C, C_e, and k were estimated by non-linear regression using Statistica 13 (TIBCO) software.

3. Results and Discussion

3.1. Effectiveness of BR46 Sorption on GB and RHs

The amount of BR46 dye bound to the sorbent was 189.4 mg/g and 125.2 mg/g for GB and RHs, respectively (Figure 5). The dye removal efficiency was 75.76% for GB and 50.08% for RHs. The parameters of the sorbents after sorption of the dye are summarized in Table 2.

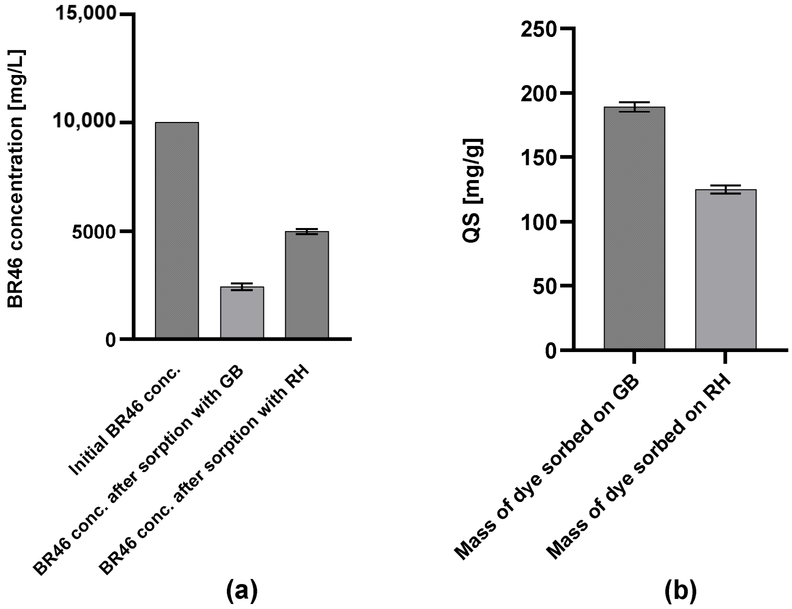


Figure 5. Concentration of BR46 in solution before and after sorption: (**a**) quantities of dye sorbed by GB and (**b**) RHs [mg/g TS].

Table 2. Parameters of sorbents after BR46 sorption.

Type of Sorbent (after BR46 Sorption)	Total Solids	Volatile Solids	Total Solids of Dye	Mineral Solids	Moisture of Sorbent
	[mg/g]	[mg/g]	[mg/g]	[mg/g]	[%]
GB	236.3 ± 10.43	162.3 ± 8.90	37.6 ± 2.39	74.0 ± 5.73	76.4 ± 4.71
RH	240.5 ± 12.98	228.5 ± 9.12	26.8 ± 3.45	12.0 ± 1.20	76.0 ± 5.16

The FTIR spectra of Canadian goldenrod [GB] and rapeseed hulls [RHs] were found to be typical of lignocellulosic plant biomass (Figure 6). Peaks at 1025 cm^{-1}, 1048 cm^{-1}, 1109 cm^{-1}, 1156 cm^{-1}, and also 1201 cm^{-1} were attributed to the C-O-C bond, characteristic of the saccharide rings of cellulose and hemicellulose [23]. Ther peak at 899 cm^{-1} indicated β-glucan glycosidic bond stretching [24]. Also typical for saccharides were peaks at 1420 cm^{-1}, 1360 cm^{-1}, and 1320 cm^{-1}, corresponding successively to stretching, bending, and ripple (wagging) vibrations—CH_2 [25]. The presence of a spar in the sorbent structure was evidenced by a distinct peak at 1630 cm^{-1} corresponding to the stretching of the C=C bond of the lignin aromatic ring [26]. Also characteristic of lignin–benzene rings was a peak at 1458 cm^{-1} corresponding to the stretching of the C-H bond [27]. The protein content of the tested sorbents was indicated by peaks at 1546 cm^{-1} and 1240 cm^{-1}, attributed successively to the N-H and C-N bonds of tertiary amides [28,29]. The peak at 1730 cm^{-1} indicated the presence of a C=O bond, which may have belonged to one of various functional groups (carbonyl, ester, ketone, and carboxyl) among the lignins [30], fatty acids, or pectins contained in the materials. The small peaks seen at 2920 cm^{-1} and

2850 cm^{-1} can be attributed to hydrophobic asymmetric and symmetric stretching vibrations of the CH_2 group of methylene side chains of lignins and also CH_2 groups of lipid chains or terminal groups of proteins [31,32]. A broad band in the range of 3600–3000 cm^{-1} was attributed to the O-H bond stretching of hydroxyl functional groups present in the chemical structure of many components of the materials tested [33]. The possession by GB and RHs of 'hydrolysable functional groups', such as amide, ester, carbonyl, and also carboxyl groups, indicated the good biodegradability of the tested materials [34–36]. The susceptibility to biodegradation was also enhanced by the presence of short aliphatic chains of lipids and protein terminal groups in the material. In addition, the spectra of the tested materials did not have peaks characteristic of toxic structures, such as sulfonic groups or halogen substituents (chlorine, bromine, fluorine), which would have negatively affected their biodegradability [36].

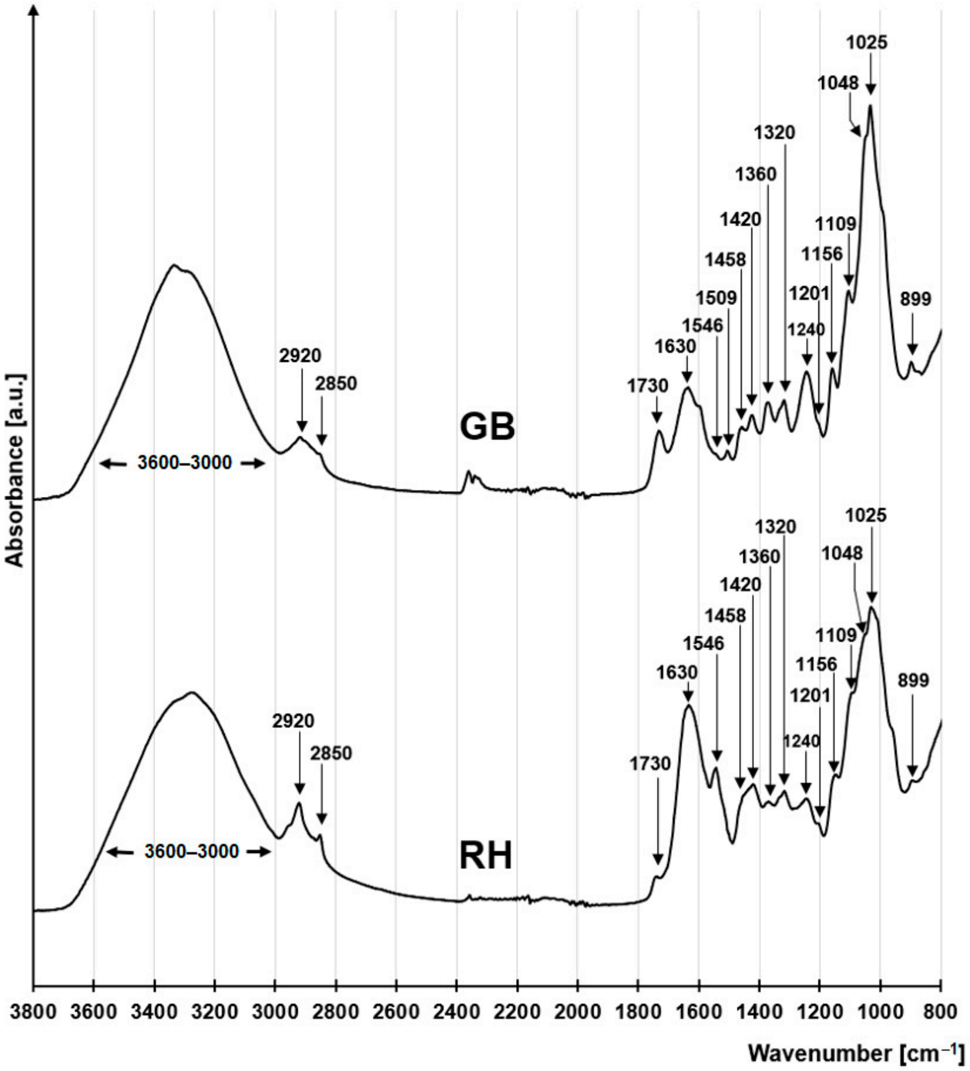


Figure 6. FTIR spectra for GB and RHs.

3.2. Physicochemical Analyses of Substrates Directed to Anaerobic Digestion

The results of the traigometric analysis of the starting substrates (Table 1) were similar to the results of other studies [37,38]. The obtained results of the chemical fractionation of fibers for GB and RHs correlated with the data available in the literature. GB data in the literature are as follows: cellulose 35–37%, hemicellulose 36–37%, lignin 18–19%, ash/ash 2–3%, protein and other components 4–9% [33,39]. According to the literature, the composition of purified RHs is as follows: cellulose 13.7%, hemicellulose 19.0%, lignin 25.0%, pectin 12.0%, protein 18.1%, other components (fats, simple sugars, ash) 12.2% [40,41]. The slight discrepancies from the literature data may have been due to a number of factors such as climatic conditions, soil conditions, fertilization, and growing season [8]. The results of substrate analyses in relation to the respiratory testing are presented in Table 3.

Table 3. Characteristics of substrates for respirometry tests.

Parameter	Shortcut	Unit	GB	GB–S	RH	RH–S
Total solids	TS	mg/g	25.07 ± 1.05	26.70 ± 1.28	24.95 ± 0.97	24.55 ± 1.53
Mineral solids	-	mg/g	7.75 ± 0.43	9.41 ± 0.27	7.76 ± 0.56	7.64 ± 0.41
Volatile solids	VS	mg/g	17.32 ± 0.98	17.29 ± 0.42	17.19 ± 0.39	16.91 ± 0.85
Chemical oxygen demand	COD	mg/L	1872 ± 74	1463 ± 51	2105 ± 67	1722 ± 49
Nitrogen	N	%	2.71 ± 0.23	2.49 ± 0.19	2.37 ± 0.31	2.79 ± 0.17
Carbon	C	%	36.81 ± 1.23	36.39 ± 0.98	38.41 ± 1.09	38.89 ± 1.17
Hydrogen	H	%	4.92 ± 0.33	4.51 ± 0.27	5.17 ± 0.20	6.18 ± 0.19
Total nitrogen	TN	mg/L	32.00 ± 15.24	31.75 ± 12.65	51.13 ± 25.02	50,75 ± 20.90
Total organic carbon	TOC	mg/L	740.75 ± 14.78	725.94 ± 15.87	711.13 ± 20.8	599.88 ± 17.89
Total carbon	TC	mg/L	1125.63 ± 32.76	1158.44 ± 26.12	1191.25 ± 34.81	1031.25 ± 29.06
Inorganic carbon	IC	mg/L	384.88 ± 10.9	432.38 ± 12.4	479.88 ± 17.13	431.5 ± 15.74
Glucose	-	mg/L	34.53 ± 0.57	28.23 ± 0.87	66.44 ± 1.34	53.72 ± 1.90
Xylose	-	mg/L	250.23 ± 13.54	220.78 ± 10.82	318.40 ± 9.15	267.69 ± 14.98

3.3. Efficiency of Anaerobic Digestion

Previously, articles have been published describing the biochemical methane potential (BMP) from invasive goldenrod varieties [42]. These studies concluded that these species are productive and inexpensive substrates worthy of interest. More extensively studied in the literature is rapeseed for energetic purposes, for the production of biogas, bioethanol, and biodiesel [43–45]. In the present study, after pre-fermentation analysis, the substrates were subjected to anaerobic digestion. Figure 7 shows a comparison of the percentage of methane in the composition of biogas obtained from Canadian goldenrod and rapeseed pomace subjected to dye sorption or not. For all samples, the largest percentage of the obtained gas was methane. Its content ranged from 64 to 69%, and the rest of the gas was carbon dioxide, meeting the value expected for methane production from plant biomass [46].

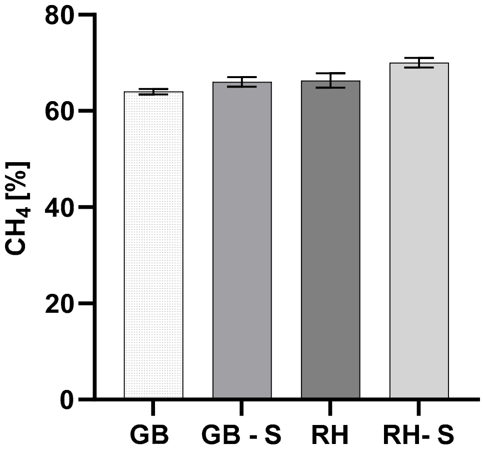


Figure 7. Content of methane in biogas.

Over the course of the study, a decrease in methane production was observed in variants using substrates after dye sorption. The decrease in production as indicated in the literature was probably due to the accumulation of volatile fatty acids (VFAs) [47]. The higher the concentration of dye, the higher the concentration of VFAs, causing partial inhibition of anaerobic processes [48]. This was confirmed by the results of our own study. In the GB-S variant, where the concentration of azo dye was higher (Figure 5), the decrease in methane production compared with the GB variant was 20%, while for RH-S compared with RHs, production decreased by 11% (Figure 8). Figure 9 shows the daily methane production for each variant of the experiment.

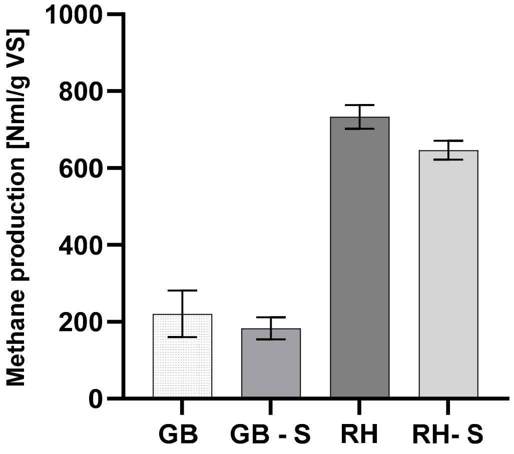


Figure 8. Final methane content.

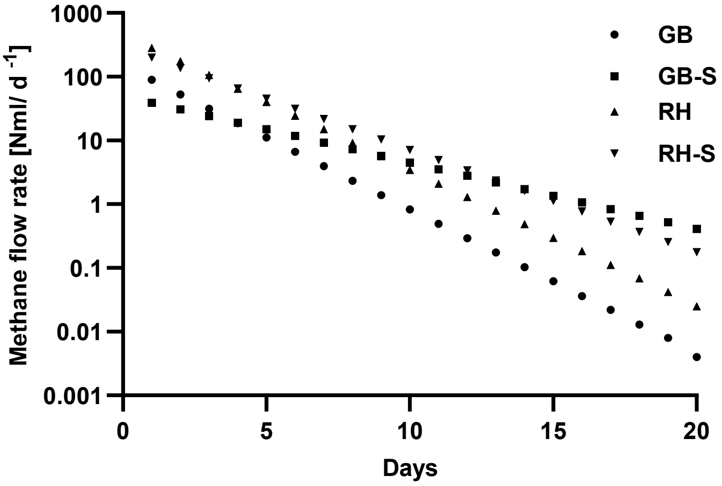


Figure 9. Daily methane production.

The amount of methane obtained from the decomposition of 1 gVS RHs was greater than the amount obtained from GB. From 1 g of VS RHs, we obtained 732.30 NmL of methane, and from 1 g VS RH–S, the quantity was 646.63 NmL. This was 11% less compared with the fresh form. From GB it was possible to obtain 220.7 NmL/gVS of methane, from GB–S we obtained 20% less methane from 1 g VS, i.e., 183.20 NmL/gVS. Studies on the usefulness of goldenrod (Solidago virgaurea), belonging to the species *Solidago* L. (goldenrod), were conducted by Oleszek and Krzeminska [37]. The suitability of goldenrod for methane production as a monosubstrate and cosubstrate for co-fermentation with corn silage was investigated. Before the fermentation process, goldenrod was dried and chopped. The methane yield from the biomass thus prepared was 127 NmL/gVS. During our own research, anaerobic digestion of Canadian goldenrod yielded 57% more methane, and for Canadian goldenrod after the sorption process, methane production was 30% higher than that of common goldenrod. Oleszek and Krzeminska in their work also reported the methane content in biogas from common goldenrod, equal to 48%. The share of methane in biogas from non-sorbed and sorbed Canadian goldenrod was 74%, so 26% more methane was obtained in the total biogas volume.

Seppälä et al. evaluated the suitability of goldenrod (Solidago gigantea) for biogas production. Prior to the fermentation process, the substrate was cut with a shredder and then cut with scissors to a particle size of about 1 cm. The biomass reactors were inoculated with inoculum from an agricultural digester processing cow manure, grass silage, and by-products from the sugar industry. From the feedstock prepared in this way, 186 NmL/gVS of methane was obtained [44].

Oleszek et al. focused on the use of silages of wild and cultivated varieties of reed canary grass (*Phalaris arundinacea* L.). The collected material was chopped and then ensiled. Anaerobic digestion of the cultivated variety of mozga showed a higher biogas yield than the wild variety. The amount of methane that could be obtained from anaerobic digestion of cane mozga silage from wild areas was, according to the authors, 120 NmL/gVS [37]. In our study, the amount of methane obtained from GB fermentation was 220.7 NmL/gVS, and that from GB–S was 183.20 NmL/gVS. The described yields from wild reed moss were lower than the obtained methane production from Canadian goldenrod.

Petersson et al. studied the efficiency of rapeseed for methane production. Pretreatment of the substrate consisted of oxidation by Na_2CO_3 at 195 °C and 12 bar pressure for 15 min. In this way, methane production of 420 NmL/gVS from rapeseed was achieved [38]. In our own research, RHs and RH-S were subjected to anaerobic digestion. They yielded 732.30 NmL/gVS and 646.63 NmL/gVS of methane, respectively.

Figure 10 shows the distribution of methane production by day of fermentation for the selected substrates. For the BMP rate (r), the highest value of 358.68 mL/d was obtained in the RH series. A high value of the reaction rate constant (k), 0.49 d^{-1}, was also observed in this series. The highest increase in methane from GB and GB–S occurred in the first five days, and the total increase occurred by day 20. The RH anaerobic decomposition curve began to flatten out after day 3 of fermentation, when the daily methane production rate began to decline. The longest fermentation time was reached by RH–S. The greatest increase in methane production occurred during the first 4 days of the process. After this period, the daily methane production decreased and the curve flattened out. Similar distributions of methane production have been observed in studies of date palm waste biomass [49]. The explanation for this can be found in the high cellulose content (Table 1), which makes GB and RHs easily accessible feedstock for methanogenic bacteria, quickly converting cellulose to simple monomers and resulting in rapid biogas production.

To determine the relationship between the use of sorption before the fermentation process and the separated sugar, COD, and CH_4 produced, Pearson analysis was performed to identify linear relationships between any two variables. Correlations were checked between 4 parameters: use or not of sorption, amount of carbohydrates (glucose + xylose), COD concentration in solution, and amount of methane produced. The statistical analysis showed that Pearson's correlation coefficient r indicated strong relationships between glucose + xylose and COD, glucose + xylose and CH_4, and COD and S. It indicated medium relationships between glucose + xylose and S, and COD and CH_4, and a weak relationship between CH_4 and S (Figure 11). The statistical test proved that the use of sorption did not have a strong effect on the amount of methane produced in the fermentation process.

From the methane production results obtained and the Pearson analysis conducted to identify linear relationships between any two variables, it was seen that despite the reduction in anaerobic digestion efficiency for the GB–S and RH–S variants, the strengths of the relationships were low. On this basis, it can be concluded that the inhibition of anaerobic digestion by VFA accumulation does not preclude the use of lignocellulosic waste from dye sorption as a potential substrate for biogas production.

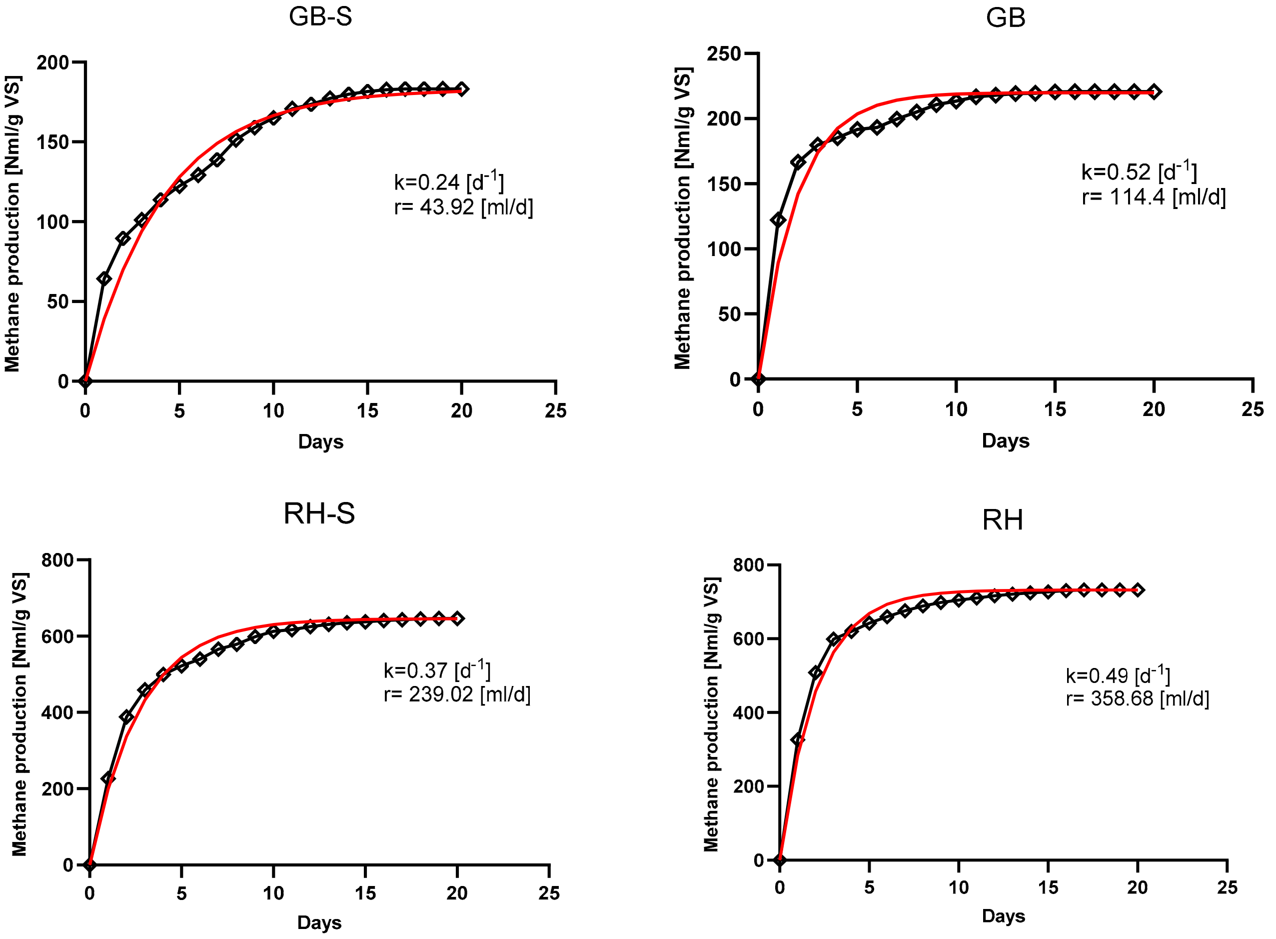
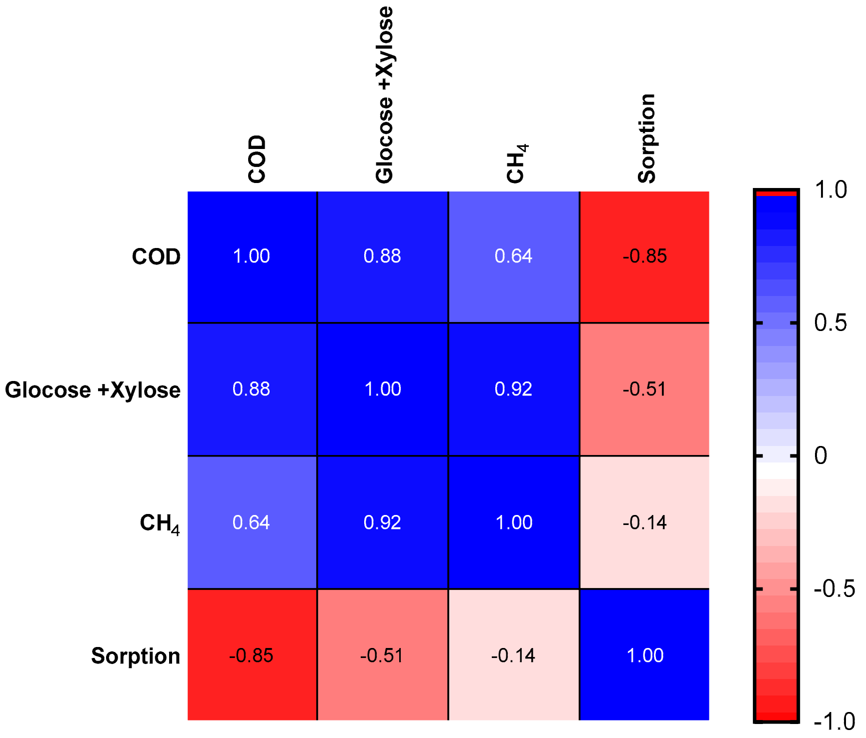


Figure 10. BMP evaluation along with the kinetic parameters of the first-order model.



	COD	Glocose +Xylose	CH_4	Sorption
COD	1.00	0.88	0.64	-0.85
Glocose +Xylose	0.88	1.00	0.92	-0.51
CH_4	0.64	0.92	1.00	-0.14
Sorption	-0.85	-0.51	-0.14	1.00

Figure 11. Pearson correlation matrix between each of the variables.

3.4. Analysis of the Digestate

Similar to the analysis of the substrates before fermentation, analysis of the chemical composition of the digestates revealed significant differences between the two plant species studied. The results obtained, along with the percentage of decrease in the values of the studied parameters in relation to the input values, are reported in Table 4. The largest decreases in values were observed for glucose and xylose, at about 99%.

Table 4. Characteristics of the digest.

Parameter	Shortcut	Unit	GB	⤓ *	GB–S	⤓	RH	⤓	RH–S	⤓
Total solids	TS	mg/g	20.03 ± 0.95	20.1	18.20 ± 0.69	31.8	16.17 ± 0.75	35.2	15.7 ± 1.11	36.0
Mineral solids	-	mg/g	7.5 ± 0.39	3.2	6.7 ± 0.18	28.8	5.7 ± 0.46	26.5	6.2 ± 0.33	18.8
Volatile solids	VS	mg/g	12.8 ± 0.78	26.1	11.6 ± 0.55	32.9	10.9 ± 0.32	36.6	9.5 ± 0.81	43.8
Chemical oxygen demand	COD	mg/L	613 ± 21	67.3	574 ± 26	60.8	597 ± 30	71.6	458 ± 24	73.4
Nitrogen	N	%	2.64 ± 0.20	2.6	2.21 ± 0.17	11.2	2.09 ± 0.22	11.8	2.4 ± 0.25	14
Carbon	C	%	34.52 ± 1.33	6.2	34.27 ±1.21	5.8	34.82 ± 1.18	9.3	35.46 ± 1.54	8.8
Hydrogen	H	%	4.74 ± 0.36	3.7	4.34 ± 0.19	3.8	4.84 ± 0.20	6.4	4.84 ± 0.23	21.7
Total nitrogen	TN	mg/L	17.0 ± 6.21	46.9	17.75 ± 4.38	44.1	25.4 ± 5.6	50.3	28.25 ± 5.16	44.3
Total organic carbon	TOC	mg/L	297.2 ± 8.34	59.9	325.1 ± 7.21	55.2	244.7 ± 6.98	65.6	226.4 ± 7.81	62.3
Total carbon	TC	mg/L	467.25 ± 21.7	58.5	495.50 ± 16.17	57.2	408.45 ± 12.87	65.7	401.74 ± 17.42	61.0
Inorganic carbon	IC	mg/L	170.05 ± 6.42	55.8	170.4 ± 5.38	60.6	163.75 ± 7.17	65.9	175.34 ± 5.25	59.4
Glucose	-	mg/L	0.56 ± 0.03	98.4	0.24 ± 0.01	99.1	0.19 ± 0.02	99.7	0.21 ± 0.01	99.6
Xylose	-	mg/L	0.23 ± 0.02	99.9	0.33± 0.02	99.9	0.08 ± 0.01	100.0	0.19 ± 0.03	99.9

* ⤓ Percentage loss in the values of the tested parameters relative to the results obtained before fermentation, summarized in Table 3.

4. Conclusions

Based on the study of the effect of sorption of Basic Red 46 (BR 46) dye by lignocellulosic biomass on the susceptibility of the waste to anaerobic digestion, a conclusion was drawn about the possibility of producing methane from the described waste. RHs turned out to be the more efficient substrate in terms of BMPs and the share of methane in total biogas production. During anaerobic decomposition of RHs and RH–S, 732.30 NmL/gVS and 646.63 NmL/gVS of methane were obtained, respectively. Biogasification of GB and GB–S resulted in methane yields of 220.70 NmL/gVS and 183.20 NmL/gVS, respectively. Sorption of the dye prior to subsequent methane digestion contributed to a reduction in the volume of methane production from lignocellulosic biomass. GB sorbent sorbed 34% more BR46 dye than the RH sorbent, which is likely to have resulted in the accumulation of VFA and contributed to the partial inhibition of methane production.

The results obtained from the volume of methane production during biogasification indicate that lignocellulosic waste from dye sorption is suitable as an energy feedstock. Not only is its use associated with obtaining a low-carbon energy source, but it also solves the problem of waste generation during dye sorption. The waste generated during the sorption process, instead of being destined for disposal or landfill, can take part in the next process, replacing typical substrates from dedicated crops. Lignocellulosic waste from dye sorption can compete with fresh biomass not previously subjected to destabilization processes. The results obtained for the production of methane from lignocellulosic waste derived from dye sorption indicate that anaerobic digestion is a favorable direction for the management of lignocellulosic waste derived from dye sorption and may prove to be a breakthrough method for its disposal.

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