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APPLICATION POSSIBILITIES OF BIOMASS FROM FENNEL FRUITS

Milena Nikolova[1], Martina Pencheva[2], Milen Dimov[3], Bozhidar Bozadzhiev[4],
Lazar Lazarov[5], Stanka Damyanova[6], Veska Lasheva[7], Albena Stoyanova[5], Nikolay Yavorov[7]

[1]*University of Food Technologies, Economic Faculty*
Department of Engineering Ecology, 26 Maritza blvd.
4000 Plovdiv, Bulgaria
[2]*University of Russe "Angel Kanchev"*
Agrarian and Industrial Department, 8 Studentska
7000 Russe, Bulgaria
[3]*Department of Food Technology, Trakia University*
38 Graf Ignatiev, 8600 Yambol, Bulgaria
[4]*University of Food Technologies, Technological Faculty*
Department of Cereals, Fodder, Bread and Confectionary Products
26 Maritza blvd., 4000 Plovdiv, Bulgaria
[5]*University of Food Technologies, Technological Faculty*
Department of Tobacco, Sugar, Vegetable and Essential Oils
26 Maritza blvd., 4000 Plovdiv, Bulgaria
[6]*University of Russe "Angel Kanchev", Razgrad Branch*
47 Aprilsko vastanie, 7200 Razgrad, Bulgaria
[7]*University of Chemical Technology and Metallurgy,*
8 Kliment Ohridski blvd., 1756 Sofia, Bulgaria
E-mail: veska_lasheva@abv.bg

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ABSTRACT

During the processing of fennel fruits (Foeniculum vulgare Mill.) for obtaining essential and vegetable oils, biomass is released. It is mainly used as an additive for feeding or as an organic fertilizer. The aim of this research is to investigate the possibilities of using biomass obtained during the processing of fruits from harvest 2020 and 2021 as a biosorbent of Cr (VI) from aqueous solutions or as a biofuel. The two biomasses were milled and the final fractions obtained by sieve analysis (between 384 and 413 μm) were analyzed. The FTIR spectrum was recorded as 4000 - 400 cm^{-1}. Both biomasses act as biosorbent under the following conditions: pH 1.0, agitation speed 300 rpm, adsorbent dose 1.05 g L^{-1}, initial Cr (VI) concentration 80 mg L^{-1}, temperature 30^oC. The energy indices used in the assessment of fennel fruit biomass potential as conditional biofuel were calculated: calorific value (15783.40 - 15968.16 kJ kg^{-1}), density (464.19 - 582.91 kg m^{-3}), and heat equivalent (250.05 - 317.68 kJ m^{-3}).

Keywords: *fennel fruits biomass, biosobent, biofuel.*

INTRODUCTION

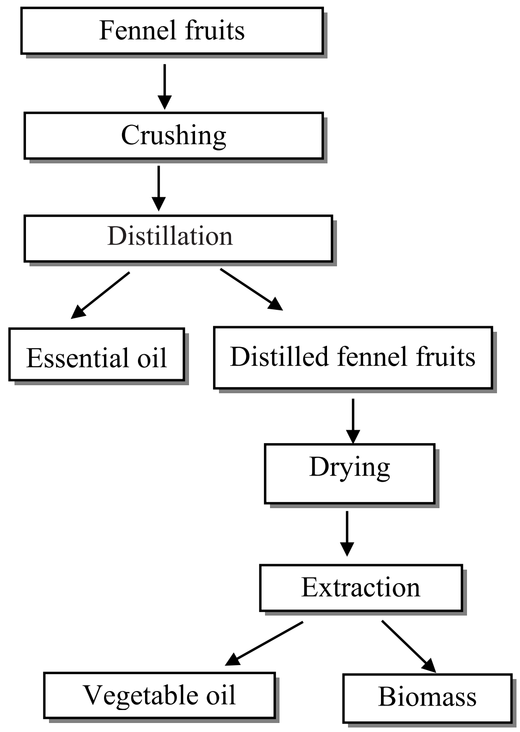
The fruits of the fennel (*Foeniculum vulgare* Mill.) contain essential and vegetable oils, which is why they are grown in different countries around the world [1]. In Bulgaria they are processed according to scheme 1 in order to obtain essential oil, which is used in the food industry and cosmetics. The remaining raw material after distillation is used as an additive to feed mixtures or for fertilizer [2]. After distillation and obtaining an essential oil from the raw material, vegetable oil can be extracted (Sheme 1) [3, 4]. The biomass that remains after the extraction of the vegetable oil also contains a variety of biologically active substances. Because of this it can be used as an additive to feed mixtures or for the extraction of proteins, flavonoids and other phytonutrients [1, 3].

In accordance with the current trends for the application of biosorption as an effective and inexpensive approach for cleaning water contaminated with heavy metals, biomass from agriculture is also used as a biosorbent [5 - 20].

According to a number of studies, biomass is the fourth energy source in the world, after coal, oil and natural gas. During the burning of agricultural waste (biomass), lower emissions of greenhouse gases are released compared to the traditionally used solid and liquid fuels. This is one of the mechanisms for regulating the planet's climate [21 - 26].

It is found that the biomass of fennel fruits can be a suitable substrate for the development of thermophilic and halophilic microorganisms [27].

The aim of the present work is to investigate the possibilities of applying biomass from fennel fruits in the two most modern and currently promising directions - as a biosorbent of Cr (VI) ions from aqueous solution and as a biofuel. This will expand the scope of application of the remaining biomass, resulting in a "closed loop", as the waste raw material will not pollute the environment.



Sheme 1. Processing of fennel fruits.

EXPERIMENTAL

Material

The annual fennel fruits (*Foeniculum vulgare* Mill. var. *dulce* Mill.) from the family Apiaceae, harvest 2020 and 2021, were used. They were provided by a company, producer of essential oil plants, located in North Eeastern Bulgaria near the town of Razgrad (43°32'00''N and 26°32'30''E).

The fruits were processed according to sheme 1, under the following conditions: hydrodistillation into a laboratory distillation apparatus according to the British Pharmacopoeia, modified by [28], duration 3 h, raw material:water ratio = 1:10. After hydrodistillation, the waste material was subjected to drying by adjusting the humidity (10 ± 0.2 %) [29].

Methods

The vegetable oil was extracted with *n*-hexane using a Soxhlet extractor [30]. Forced air circulation (0.2 m s^{-1}) was provided in the drying rooms (25°C), ensuring even drying and avoiding the development of molds. The biomass was separated on sieve bases and was periodically stirred mechanically during the drying process.

Physical and chemical characteristics

The biomass was crushed on a Schule laboratory pin mill (Germany) at a peripheral pin speed of 64 m s^{-1} and a load of 30 kg h^{-1}. Sieve analysis of the crushed product was performed according to BSS 754 [29]. The distribution density was determined according to the methodology of DIN 66 141 [30]. In order to achieve the required degree of grinding of the final product, additional grindings were made, and the fraction between 384 and 413 μm was used for further analyzes.

Cellulose, ash and moisture were determined using methods described in AOAC [31]. All values were represented on the base of absolute dry weight. The density was determined by a picnometer [33]. The infrared spectrum was recorded using a Nicolet iS 50 (Thermo Scientific, USA) FT-IR spectrometer in the frequency region of 4000 - 400 cm^{-1}, with the samples embedded in KBr matrixes.

Biosorption

All reagents used in the experiments were of analytical grade. Stock solution (500 mg L^{-1}) of Cr (VI) was prepared by dissolving of $K_2Cr_2O_7$ in distilled water.

This solution was diluted with distilled water to obtain desired concentrations of working solutions for the batch experiments study. The pH value of the samples was adjusted by adding 0.1 M NaOH or HCl solutions [34].

Biosorption experiments were carried out in 250 mL Erlenmeyer glass flasks with 100 mL volume of Cr (VI) solution, as described in our previous studies [34, 35]. Batch experiments were conducted to investigate the effect of pH (1.0, 2.0, 3.0, 4.0, 5.0, and 6.0), agitation speed (150, 200, 250, 300 and 350 rpm), biosorbent dosage (0.1, 0.2, 0.5, 1.0, and 1.15 g L^{-1}), and initial Cr (VI) concentration (20, 40, 60, 80, 100, and 150 mg L^{-1}). The values of investigated factors were selected from a practical point of view and based on the literature review [34, 35].

For determination of Cr (VI) concentration in the solutions before and after biosorption, samples were vacuum filtered (MN640 de filter paper) and the filtrate was analyzed spectro-photometrically at 540 nm by using the standard diphenilcarbazide method [36].

The equilibrium metal uptake q_e (mg g^{-1}) was determined by employing the mass balance (1) [34]:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where: C_0 and C_e - the initial and the final metal concentrations (mg L^{-1}); m - the mass of biosorbent material (g); V - the initial volume of Cr (VI) solution (L).

The performance of biosorption was evaluated in terms of its removal efficiency as RE (%), estimated by the following equation (2):

$$RE = \frac{(C_0 - C_t)}{C_0} . 100 \tag{2}$$

where C_t - the Cr (VI) concentration at time t [34].

Energy indices

The heating value (kJ kg^{-1}), density of wood biomass (kg m^{-3}), and heat equivalent (J m^{-3}) were calculated according to the method [37].

Statistical analysis

All experiments were carried out in triplicate at ambient temperature 30.0 ± 1.0°C. The data were analyzed and presented as mean values. Statistical techniques, incl. ANOVA and Duncan's Multiple Range Test were applied to determine the significant differences at 95 % confidence ($p < 0.05$) level.

RESULTS AND DISCUSSION

Physical and chemical characteristics

The characteristics of fennel fruit biomass are predented in Table 1. In the literature the values of moisture are not higher than 8 %, and those of ash - up to 4 %. The results in our study showed that values for ash content were higher than those presented for other wastes (1.3 %) [38] and (0.59 - 2.69 %) [39]. Higher values of ash content reduced the calorific value of biomass [37]. It is known that lignocellulosic biomass has a low ash content (0.2 - 1.8 %), which is considered as a guarantee for the absence of slag, which is formed in biogenic fuels containing more than 4 % ash. The cellulose content is lower compared to wood species that are mainly used as biofuels.

The particle size distribution of the crushed biomasses from 2020 and 2021 is presented in Fig. 1. A tendency towards an increase in the mass with an increase in the sizes of their particles was reported. The differences between the mass fractions of the two years range between 1.7 and 26 %. The mean particle diameter of the biomass in 2020 was 882 µm and in 2021 it was 1110 µm. This was was due to the 1000 - 2000 µm class, distinguished by the largest mass fractions from both years.

The distribution density of the crushed biomasses from 2020 and 2021 is presened in Fig. 2. The distribution density of the fractions was uneven, considering two maximum values in the values in the 150 - 280 µm class and in the 800 - 1000 µm class for

Table 1. Physical and chemical characteristics of fennel fruit biomass.

Index	Moisture, %	Ash, %	Cellulose, %	Density, kg m^{-3}
Biomass 2020	10.13 ± 0.09	5.02 ± 0.04	37.22 ± 3.50	0.4954 ± 0.0
Biomass 2021	9.03 ± 0.08	5.00 ± 0.04	32.97 ± 3.00	0.5871 ± 0.0

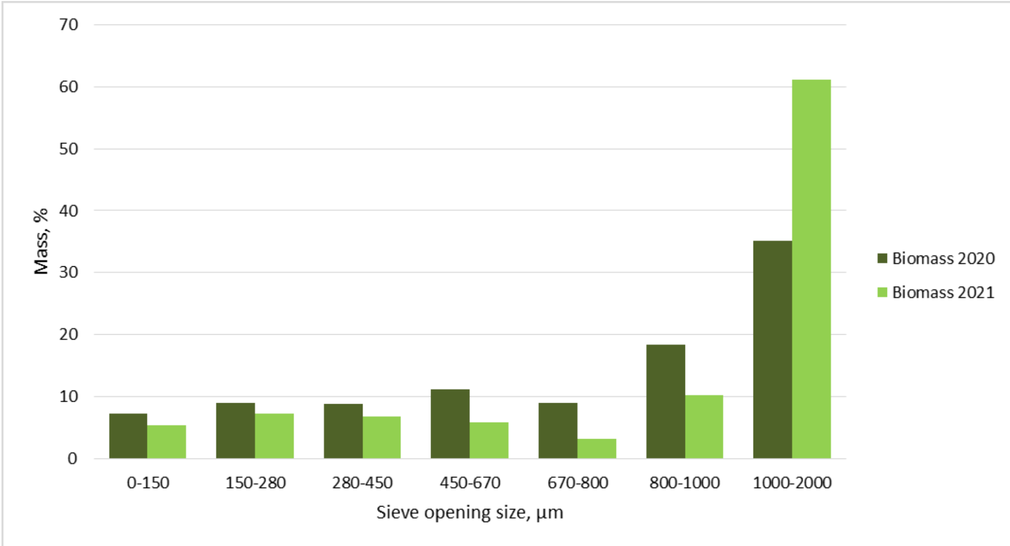


Fig. 1. Partical size distribution of crushed fennel fruit biomass.

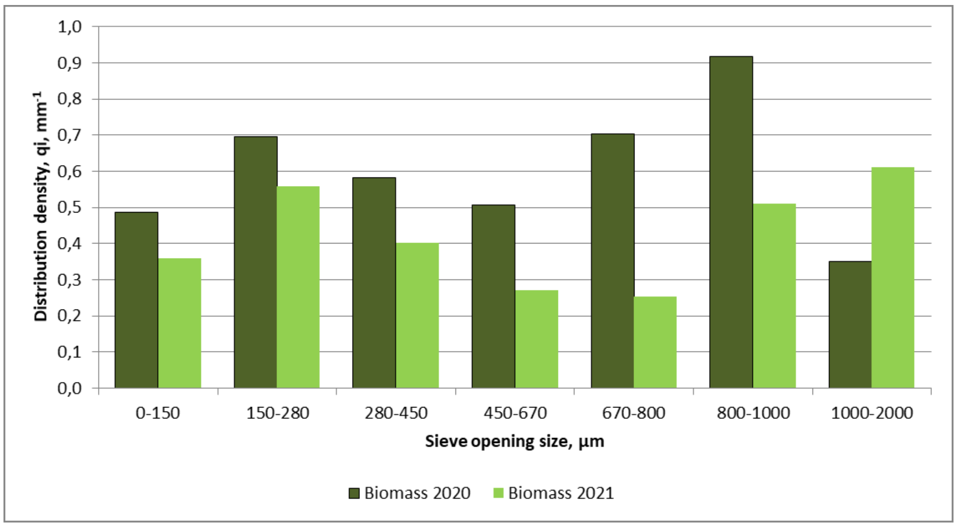


Fig. 2. Distribution of fractions of crushed fennel fruit biomass.

both years. This shows that the distribution is bimodal and non-symmetric about the y-axis.

The grinding process and the granulometric evaluation of the biomass provided information on the degree of fragmentation of the particles during the following procedure, for example during the production of the pellets in the presence of pressure. Particle size was one of the important factors influencing the properties of particulate materials, and having a great impact the quality and on the utilization of the final product. In case of plant biomass, particle morphology is greatly irregular [40]. The crushing (milling) process is a necessary step in suspension firing. Biomass is, due to its fibrous structure, difficult to mill. Size reduction improves fuel conversion processes because of the creation of larger reactive surface areas [41]. The size of the biomass digestion corresponds to the digestion rates recommended by other authors for biomass from plant species used for pellet production [42].

FT-IR analysis of the two biosorbents was carried out in order to identify the functional groups involved in the removal of Cr (VI) from aqueous solutions. The results are presented in Table 2, Fig. 3, and Fig. 4.

All two samples contained OH group, which was

Table 2. Assignments of the characteristic bands in the FT-IR spectra of biomass from fennel fruits.

Characteristic bands, cm^{-1}			Group type
Biomass 2020	Biomass2021	Reference data	
3412	3421	3550 - 3400	γ OH intramolecular H-bond
-*	2925	2940 - 2915	γ_{as} $-CH_2$-group
2360	2360	3110 - 2342	vibration of γ (OH) bond
-	1734	1775 - 1700	R-CHO ν C=O; characteristic band of carbonyl group
1654	1654	1665 - 1635	a characteristic band for cis- HRC = CR'H bond
1508	1507	1525 - 1475	a characteristic band of the type ν C=C
-	1457	1465 - 1440	$-CH_2$-CO– vibrations of ketones, δ CH_2
1089	1096	1150 - 1050	γ_{as} C-O-C, ether bond
983	-	990 - 960	Trans double bond, γ =C-H

** not detected.*

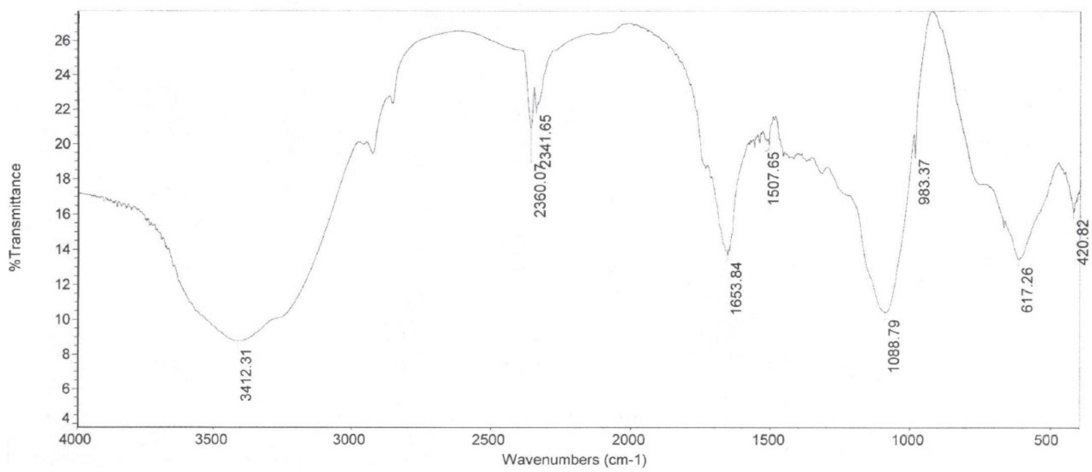


Fig. 3. FT-IR-spectrum of biomass 2020.

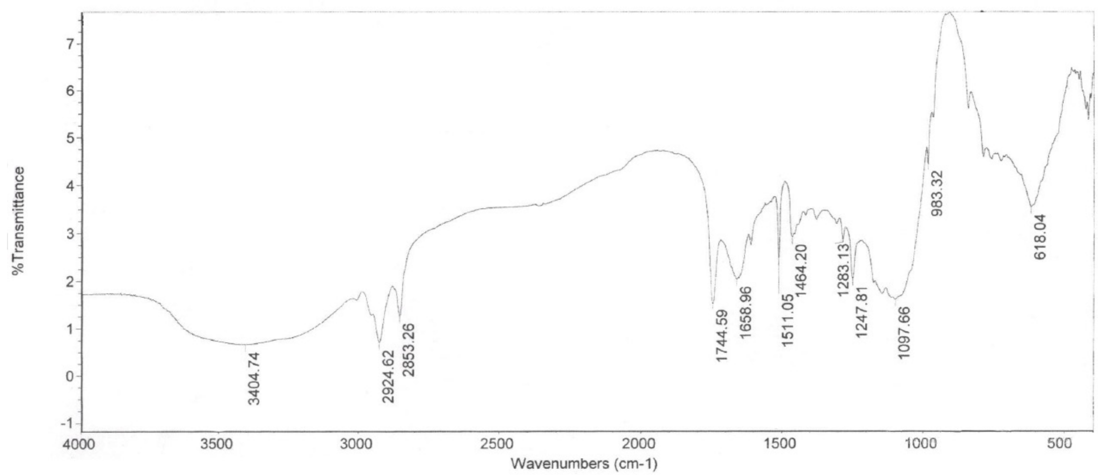


Fig. 4. FT-IR-spectrum of biomass 2021.

confirmed by the absorbtion bands: for biomass 2020 (3412 cm^{-1} and 2360 cm^{-1}) and for biomass 2021 (3421 cm^{-1} and 2360 cm^{-1}). For biomass 2021, an absorbtion band appeared at 1734 cm^{-1}, a characteristic band for an aldehyde carbon group. Both samples have characteristic absorbtion bands for cis- a double bond of the type HRC=CR‘H, respectively at 1654 cm^{-1}. The two samples have absorbtion bands at 1508 cm^{-1} and 1507 cm^{-1}, characteristic of an aromatic nucleus band (oscillations for γ C=C). It was noteworthy that in both samples there were no characteristic γ C-O-H bond type bands (hydroxyl group) at wavelength of 1283 cm^{-1}. Also, a characteristic band for an ether bond of the γ_{as} C-O-C type, at a wavelength of 1248 cm^{-1}, was also absent. This may be due to the thermal effect on these bonds during the distillation of the fruit, where the temperature was 100°C. Additionally some bands typical for carbohydrates, especially lignin and cellulose were observed (Table 2). This could be explained with cellulose content in samples. A band around 1457 cm^{-1} observed due to deformation of lignin CH_2 and CH_3 and 1636 cm^{-1} was typical for stretching of the C=C and C=O lignin aromatic ring. A band at 1735 cm^{-1} was assigned to C=O stretching of unconjugated hemicellulose while the band at 2925 cm^{-1} was due to asymmetrical stretching of CH_2 and CH. Our observation coincided with the bands reported in literature which denoted the characteristics of cellulose [42]. The obtained diffraction peaks corresponded to the previously reported and showed the difference in the intensities of the peak maxima in the two biomasses [43, 44].

Biosorption

The data from Table 2 show that both biosorbents possess functional groups available to bind Cr (VI) ions. The influence of various factors on the extraction of Cr (VI) ions from aqueous solutions was investigated - pH, amount of biosorbent, initial concentration of metal ions.

The pH of aqueous solutions is an important parameter because it determines the surface charge of the sorbent and the degree of ionization of the sorbate during adsorption [8]. Therefore, the determination of the optimum pH value, i.e. the one in which the maximum possible extraction of the metal was obtained is very important from a practical point of view [20]. The influence of pH (1.0, 2.0, 3.0, 4.0, 5.0, and 6.0) on the extraction of Cr (VI) from aqueous solutions with the two biosorbents studied is presented in Fig. 5. The results show that the maximum cleaning efficiency is found at pH 1.0, respectively: 32.43 % and 45.42 % for biomass 2020 and biomass 2021. This is consistent with previous studies that also found maximum removal of Cr (VI) at pH 1.0-2.0 for various biosorbents. It is known that at low pH chromium is found mainly as negatively charged $HCrO_4^-$ and the positively charged surface of the adsorbent under these conditions favors the sorbent-sorbate interaction leading to effective retention of Cr (VI) [7, 9, 10, 12].

The removal of Cr (VI) as a function of agitation speed was studied by varying the speed (150, 200, 250, 300 and 350 rpm) (Fig. 6). Increasing of the agitation speed up to 250 rpm results in improvement of the diffusion toward the biomass surface and increases the

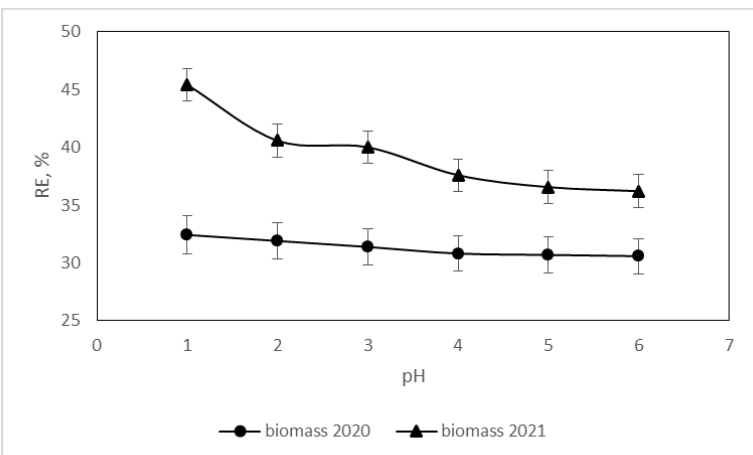


Fig. 5. Effect of pH on the removal efficiency of Cr (VI) from aqueous solution by biomass from fennel fruits (initial metal concentration 100 mg L^{-1}, biosorbent dosage 0.1 g, 30°C, 60 min, agitation speed 200 rpm).

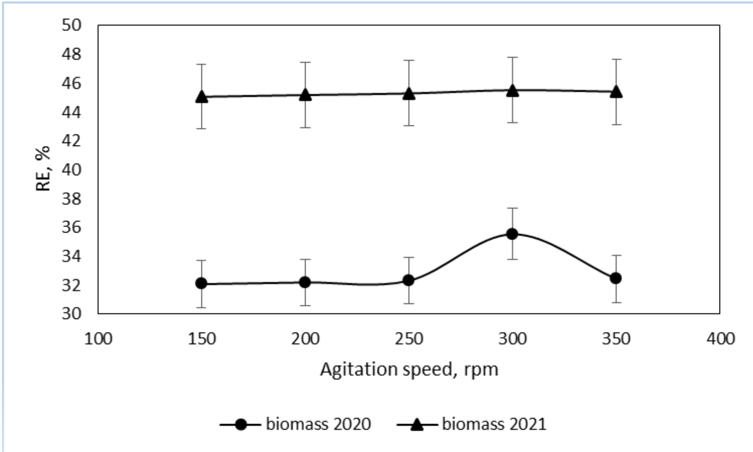


Fig. 6. Effect of agitation speed on the removal efficiency of Cr (VI) from aqueous solution by biomass from fennel fruits (pH 1.0, initial metal concentration 100 mg L^{-1}, biosorbent dosage 0.1 g, 30°C, 60 min, agitation speed 200 rpm).

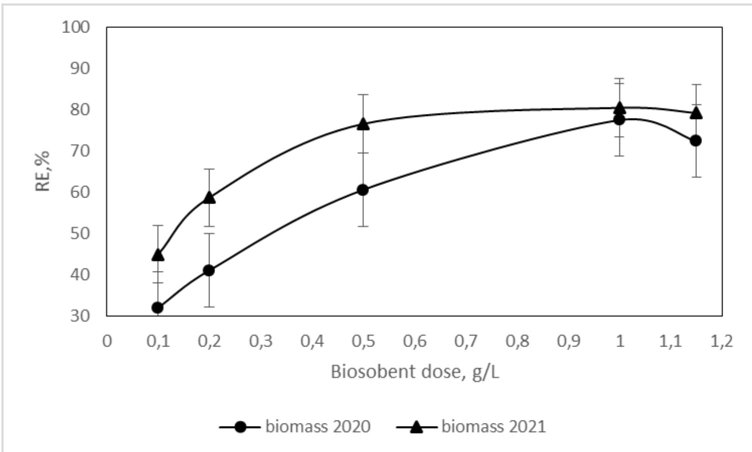


Fig. 7. Effect of biosorbent dose on the removal efficiency of Cr (VI) from aqueous solution by biomass from fennel fruits (pH 1.0, initial metal concentration 100 mg L^{-1}, 30°C, 60 min, agitation speed 300 rpm).

metal removal efficiency. Then increasing of the speed above 250 rpm lowered the metal removal, not allowing enough time for metal ions to adsorb [13, 16, 17].

The results for the extraction of Cr (VI) from aqueous solutions by biomass 2020 and biomass 2021 as a function of the amount of biosorbent dose (0.1, 0.2, 0.5, 1.0, and 1.15 g L^{-1}) are presented in Fig. 7. The extraction efficiency of Cr (VI) increases with an increase in the amount of biosorbent up to 1.0 g L^{-1}, then decreases, more pronounced at biomass 2020. The increase in efficiency is explained by the increase in the contact surface and the presence of more points for sorption, also indicated in previous studies [9]. Increasing the amount of biosorbent above 1.15 g L^{-1} at a fixed particle size and stirring speed leads to a decrease in the extraction efficiency of metal ions, due to the formation of aggregates from the biosorbent particles and disturbance in the mass transfer of metal ions from the liquid to the solid phase. This effect was reported similarly by other studies [12 - 17, 45].

The results of the influence of the initial concentration (20, 40, 60, 80, 100, and 150 mg L^{-1}) of Cr (VI) in the solution on the extraction efficiency of the metal ions are presented in Fig. 8. The range of variation of the initial concentration of Cr (VI) in the solution was chosen from a practical point of view, given the fact that conventional industrial wastewater treatment methods are not effective at a concentration of Cr (VI) from 20 to 150 mg L^{-1}. The highest extraction efficiency (89.20 and 88.20 %) was found at an initial metal ion concentration of 80 mg dm^{-3} for biomass 2020 and biomass 2021, respectively. The extraction efficiency of Cr (VI) ions decreases with an

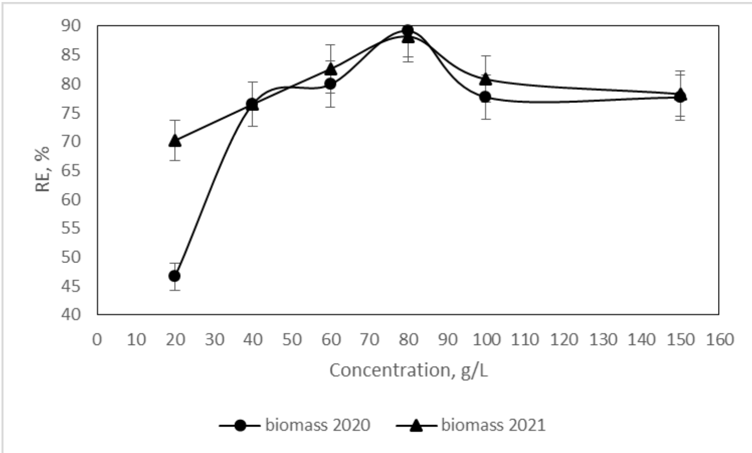


Fig. 8. Effect of initial concentration of Cr (VI) from aqueous solution by biomass from fennel fruits (pH 1.0, initial metal concentration 100 mg L^{-1}, 30°C, 60 min, agitation speed 300 rpm).

Table 3. Energy indices of biomass from fennel fruits.

Bio mass	Calorific value, kJ kg^{-1}	Density, kg m^{-3}	Heat equivalent, kJ m^{-3}
2020	15783.40	464.19	250.05
2021	15968.16	582.91	317.68

increase in the initial concentration of metal ions, due to blocking or saturation of the active groups of the biosorbent, also indicated in previous studies [12 - 17].

The results show that, in general, biomass 2021 is a more efficient biosorbent of Cr (VI) compared to biomass 2020.

Biofuel

The calculated energy characteristics are presented in Table 3.

The data showed that the calorific values obtained for two samples in this study were lower than the data in the literature for other biomass (16.53 - 18.13 MJ kg^{-1}) [46]. Biomass density values obtained in this study were lower than that reported in the literature for other biomass (above 650 kg m^{-3}) [46, 47]. The differences could be explained by the origin of the raw material, the size of grinding, moisture and ash content of the plants. The results show that, in general, biomass 2021 has better energy performance compared to biomass 2020. The energy characteristics of both biomasses can be increased if other raw materials are added to them, for example wood biomass.

The observed differences in the properties and the indices in the studied biomasses from two harvests can be explained by the climatic conditions of growing the plants, regardless of the fact that they are from the same region, which was also found in other plants [1, 2].

CONCLUSIONS

The possibility of applying biomass from fennel fruits as a biosorbent and biofuel was studied. The results from the present study demonstrated clearly that the fennel fruit biomass obtained by distillation of essential oil and extraction of vegetable oil can be used as a percentage in the composition of bioenergy composite mixtures. Biomass can also be used as a biosorbent of Cr (VI) from aqueous solutions.

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